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EDITORIALS

THE CHAPIN REPORT

The report of Mr. E. S. Chapin, Paris representative of the Textile Alliance, Inc., published on page 1130, will prove extremely interesting reading to all who are following the disposition of German dyes under the terms of the Peace Treaty.

While the report was prepared primarily for the Textile Alliance and for the consumers and producers of dyes, its reading will repay all chemists, for it gives an exceedingly clear and concise review of the progress made in the distribution of German dyes, and points out the problems still awaiting settlement, problems which will eventuate as policies to be pursued during the next five years.

During his stay in Europe, Mr. Chapin attended all of the interallied conferences on dyes, was in frequent consultation with the leaders of the German industry, had constant access to accurate records, and was in Germany a number of times. For these reasons his report bears a stamp of authoritativeness which marks it as a most valuable contribution to the literature of this much-beclouded subject.

Aside from the explanatory sections of the report, there are three features of especial interest:

First—Mr. Chapin comments on "the change in the attitude of the Germans from apparent hostility to active coöperation with the Textile Alliance." This is simply another tribute to the efficiency, unselfishness, and fairness of that remarkable organization which has handled so large a volume of business for the Government throughout the war period, without one cent of profit or remuneration.

Second—To those who made such outcry a year or more ago that American textile interests were suffering severely from the influx of British goods dyed with German dyes unobtainable in this country, it must come as a distinct shock and doubtful relief to learn that "Great Britain had secured on the free market up to August 1 [1920] 200 tons of dyes. This should be compared with our figure of 400 tons as of September 7 [1920], plus the unknown quantity imported into the United States under license through other channels."

Third—The most illuminative section of the report is that bearing on the qualitative and quantitative output of the German dye plants from February to July of this year. In spite of the much-talked-of scarcity of coal and difficulties with labor, the output increased from ten to thirty-three and a third per cent of normal. The report adds: "while the production of the vat and alizarin type dye is increasing slowly from 228 tons in May to 261 tons in June and 272 tons in July, *the production of the type of dyes made in the United States is increasing by leaps and bounds* [italics are ours] from 2400 tons in May to 2800 tons in June and 3800 tons in July."

Squelch the Moses-Thomas opposition, Senators, and pass the dye bill in the form your Committee on Finance reported it!

LYING DOWN ON THE JOB

We have received a communication, printed in full, page 1132, from Mr. N. E. Franklin, president of the Kny-Scheerer Corporation of America, called forth by the editorial in the September issue entitled "Crippling a Great Work."

Mr. Franklin feels that some one took advantage of our good nature. Wrong, Mr. Franklin, entirely wrong. That editorial was inspired solely by a knowledge of the public hearing held in Washington (not the first hearing, but a second hearing before the full Senate Finance Committee), at which was disclosed the character of the opposition to the Bacharach bill, which places a protective duty on a number of war-born American products, among them surgical instruments. Mr. Franklin, who was treasurer of the Kny-Scheerer company, is doubtless aware of the opposition to the bill shown on that occasion by Mr. Brand, the then and now vice president of his company, as set forth in the brief filed with the Committee. He doubtless knows that Mr. Richard Kny, the then president and, we understand, now consulting director of the company, was also present.

In the light of this opposition it needed only a superficial investigation to learn that the Kny-Scheerer company had reverted entirely to the business of importing, having closed their Brooklyn plant. Mr. Franklin thinks that the general public is not interested in this. We take it as a matter of very grave public interest that the country is reverting to that condition which existed at the beginning of the war, when we were unable to supply adequate quantities of instruments not only to our civilian hospitals, but even to the very surgeons who were preparing to embark for France with our Army.

Mr. Franklin protests that his company is "owned and controlled solely by born Americans." Of course. That was the whole point of the editorial. He continues, these are "men who lent their services in many ways to their government during the recent great struggle." We do not doubt it; but we were criticizing not what they did during the great struggle, but since its close. *Nowhere in Mr. Franklin's letter is a single word of denial of any fact set forth in our editorial:* namely, that Mr. Kny, whose activities as a German propagandist had been so clearly set forth in the official report of the Alien Property Custodian, was retained by the American owners as president for at least a year; that Mr. E. S. Beck was retained as secretary (in this connection it is worthy of record that Mr. Beck is a brother-in-law of Mr. Scheerer, of the Jetter & Scheerer Co., of Tuttlingen, Germany, and is still secretary of the Kny-Scheerer Corporation of America, which is the sole agent in this country of the German company); that the manufacturing plant in Brooklyn is closed; and that the goods of this company were offered to consumers at figures 20 per cent below American prices. Nowhere in Mr. Franklin's letter is there any intimation that his company is planning to develop an American surgical instrument industry. It is a tacit acknowledgment that his concern is not interested in the task of continuing the development of American workmen skilled in this art, but prefers to make dividends by importing German wares. If this is not crippling a great work, then the term American economic independence is a hollow mockery. Meanwhile, we know that American workmen have recently vainly sought employment of the character they were engaged in before the renewal of German importations, that some manufacturers who had begun the manufacture of surgical instruments have been compelled to decrease by half the number of their employees, while others have quit the field entirely.

If the Kny-Scheerer Corporation of America is to continue merely an importing agency, if it is to do no constructive service in the development of an American industry, then it was a sad day for America when the Alien Property Custodian allowed this fine property to be sold to its present American owners. In the light of Mr. Franklin's own letter we are, to our regret, confirmed in the conviction that they have lain down on the job.

THE MASQUERADING FILTER PAPER

It seems to be the season for presidential letter writing. Here is another, duly published on page 1132,—this time from Mr. Herman A. Holz, president of Holz & Company, Inc., protesting against what he considers "erroneous statements published on page 955 of the Journal in reference to the 'Franklin Filter Papers' which caused so much unpleasantness at the recent Chemical Exposition."

Why does Mr. Holz write us and at such length? Holz & Co., Inc., were not mentioned in THIS JOURNAL, nor did they make any exhibit of Franklin filter paper. The display was made by the Rohde Laboratory Supply Company, and neither on its advertising leaflet, on the labels of the packages, nor on the boxes, was there any word as to German origin. In marked contrast stood out the exhibits of French and English papers shown at the Exposition. These bore on their respective labels *Made in Paris* or *Made in England*, without the slightest suggestion of dissemblance.

We know nothing of the "young business man" to whom Mr. Holz refers. Many complaints about the exhibition of Franklin filter papers came to us, in the capacity of Chairman of the Advisory Committee, during the latter part of Exposition Week. Confirmation of the German origin of the Franklin filter papers was given by Messrs. H. F. Coors and A. A. Campbell, who questioned the attendant in charge of the Rohde exhibit. Mr. Coors has confirmed our memory of his statements:

> "Telegram received. Conversation practically verbatim as follows: *Question:* I did not know analytical filter paper was made in America. No reply. *Question:* Is this made in America? *Answer:* No. *Question:* Where is it made? *Answer:* Germany. *Question:* Whom by? *Answer:* Schlucher and School [Schleicher and Schüll]. *Question:* Where in Germany? *Answer:* Dueren. This was followed by the attendant in charge offering to send me samples. My reply was to the effect that I would secure the paper through the regular channels.—H. F. COORS."

Mr. Campbell confirms this statement, for he writes us:

> "Upon question by Mr. Coors as to where the paper was made he [the attendant] seemed very reluctant in making the statement of it 'being made in Germany,' however, after the writer led him on, he told us that it was a product of 'S & S' of Dueren."

So it was not "S & S" after all, according to Mr. Holz. The coaching of the attendant seems to have been poorly done.

Finally, Mr. Holz naïvely says, "The reason for the change of label was only the difficult pronunciation of the manufacturer's name: Macherey, Nagel & Co." Why not have tried "M & N?" We are accustomed to abbreviations on German filter papers.

SUBSTANCE RATHER THAN SHADOW

A correspondent writes us in protest against the recent action of the Council advising local sections to refrain from joining local engineering and technical societies. He feels that "the idea of the parent Society trying to hamper such affiliations by resolutions passed is, in my mind, non-progressive and rather reactionary." He contends that "technically trained men, would they be chemists, civil engineers, mining engineers, or other men of similar qualifications, would naturally associate together for the purpose of furthering matters which they are especially able to further and making themselves, in this way, more felt in the community than they are at present."

Is not our correspondent confusing the substance and the shadow? Council action was taken because of direct reports from councilors that local sections had frequently been committed to policies directly in opposition to those of the parent Society and also to the convictions of a majority of their own members. Certainly such experiences make an uncomfortable and undesirable situation. That is the shadow.

On the other hand, no one will take issue with our correspondent on the desirability of mutual association on the part of technically trained men in any community. That is the substance. To gain this it is not necessary to effect a union of local sections of national organizations, but to bring together all the technically trained of a community in a purely local organization. This has been done very successfully in Indianapolis through the medium of the *Scientech Club*. This club, made up of professional, scientific, and technical men, seeks

1. To give the City of Indianapolis and the State of Indiana the benefit of the united scientific and technical knowledge and experience of its members.
2. To promote scientific and technical research.
3. To unify and coördinate the activities of the various scientific and technical societies of the State of Indiana.
4. To maintain a high professional standing and further acquaintance and fellowship among scientific and technical men.

The various groups of technically trained men are represented on its directorate, and committees carry on active work on city planning, rail traffic, food and nutrition, public health, fuel conservation and smoke prevention, research, professional ethics, patents, daylight saving, education, and highway traffic. The club holds monthly meetings and issues a monthly bulletin.

There is the real substance of association of local technical men for mutual benefit and the good of their community. Meanwhile the Indiana Section of the American Chemical Society continues as a prosperous organization, busy with its own special problems, unfettered and unembarrassed.

EVOLUTION IN ALCOHOL ADMINISTRATION

Alcohol, the chemical reagent, is to receive some meed of that official administrative consideration which Congress intended at the time the National Prohibition Act was passed. Since the public hearing before the Bureau of Internal Revenue last summer Commissioner Williams has been thoroughly sympathetic, but inadequate funds for the administration of the Act and the onerous work involved in enforcing the prohibition feature have made the problem difficult of solution.

According to announcement from Washington, the former Division of Technology has been replaced by a Permit Division, in charge of Dr. A. B. Adams, and an Industrial Alcohol and Chemical Division, in charge of Dr. J. M. Doran. The fact that these competent chemists, both of whom have been connected with the Bureau for several years, are to have charge of the new divisions, will inspire confidence and a desire to coöperate.

The Permit Division will have general administration of the features of Title II of the National Prohibition Act, relating to permits, bonds, etc. Strength to Dr. Adams in eradicating falsified applications for withdrawal of alcohol, and wisdom in eliminating the aggravating requirements which now beset those who are acting in good faith!

The Industrial Alcohol and Chemical Division will have jurisdiction of (1) the general administration of all the features embraced in Title III of the Act, with particular reference to tax-free alcohol, (2) the development of uses of denatured alcohol by laboratory work and research, (3) the supervision of construction and operation of industrial alcohol and denaturing plants and bonded warehouses, and control of government offices assigned thereto, (4) the laboratory examination of articles manufactured under Section 4 of Title II of the Act, and (5) the examination of samples obtained under the Harrison Narcotic Act. To Dr. Doran and his associates there is entrusted the development of a work which contains untold potentialities for our chemical industries, if carried out in a thoroughly efficient manner. It is to be hoped that Congress will provide adequate funds to insure maximum results.

The method of the evolution of this administrative change gives genuine satisfaction. The matter was presented earnestly but dispassionately by those to whom injustice was being done, and was received courteously and sympathetically by the authorities in Washington. Now the apparent difficulties have been overcome, and adjustments made which will open a new chapter in national chemical development.

NOTES

The London letter was unfortunately received too late for publication in this issue.

The Patent Office, which for some time past has been handicapped by a shortage of funds and personnel, is now in position to resume the furnishing of photostatic prints of the specifications and drawings of foreign patents.

The new chemical laboratory fever has struck New England. Dartmouth College is expending from $350,000 to $400,000 on such an addition to its campus. At Yale University plans for a new building for its Department of Chemistry are practically completed.

We must confess to having received a severe jolt, in spite of our usual optimism, when a correspondent recently wrote that he had resigned his position because "the company was engaging a *physician* to act as head of the chemical laboratory."

Chemistry is not being neglected by the Swan family. While Dr. J. N. Swan heads the department at the University of Mississippi, his three sons are in training for the profession. Stewart D. holds a du Pont Fellowship in the University of Chicago, William O. has won a similar honor at the University of Virginia, and Thomas H. holds an assistantship as a graduate student in Columbia University. That's not a "bunch" of chemists—it's a whole flock.

The success of the technical monographs now under preparation by the American Chemical Society depends on one thing—how far the heads of industrial concerns will allow their chemists to "open up." Lasting contributions to chemical literature, helpful to the entire chemical industry, should be made through these monographs. Here's hoping!

With so large a number of real specialists on explosives in government service and out of it, why did the Department of Justice call upon Walter T. Scheele for an exhaustive report on the Wall Street explosion? True, he had one receipt for an explosive mixture which he put to diabolical purpose in blowing up ships during the war, but this scarcely constitutes a claim for preëminent qualifications as an expert, especially in view of the evidence of his lack of ability as an explosives expert obtained by chemists in the government service during his internment. Suppose the Department of State should call on von Igel or von Papen to solve some of its problems!

CHEMICAL INDUSTRY AND TRADE OF SWEDEN

By O. P. Hopkins

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Weighing all the disadvantages of her position during the war against the advantages, it must be admitted that Sweden's industries have been greatly strengthened since 1914. She has sold her products to both belligerents at handsome profits and has received the highest returns from her shipping in spite of losses by submarines.

Sweden's sources of wealth lie in her forests, in her iron mines, in her waterpower, and in her shipping facilities. Agriculture is also of first importance, one-half the population devoting itself to that branch of industry, although agricultural products do not figure largely in the country's international trade. One-half of the land is covered with forests, and before the war the income from that source was $100,000,000 a year. Eighty per cent of the total exports are derived from forest and mine. Waterpower is so abundant and cheap that electric current is the power used for more than half of the manufactured products of the country. It is estimated that the potential waterpower is 6,000,000 turbine horsepower, of which something more than 1,000,000 horsepower is now utilized.

Sweden has never occupied the place in the estimation of American business men that its wealth and good will toward America deserve. More attention has been given to Swedish facilities for handling trade between America and other countries than to its own trade. During the war, however, the United States entered into closer and more extensive business relations. American goods are very well liked, and the old good will toward America, the natural result of having so many sons living and prospering in this country, has not been altered.

FOREST PRODUCTS

Swedish forest products have a world-wide reputation. The timber is sold in many markets, often in competition with the American article, and while some varieties are admittedly inferior to corresponding American timber in quality, this is more than offset in many cases by the care with which it is prepared to meet the requirements of the foreign buyer.

The wood pulp manufactured in Sweden has a deservedly high reputation everywhere and is produced to the extent of considerably more than a million tons a year, of which the finest chemical pulp is largely exported, while much of the cheaper pulp is manufactured into paper in the country. The difficulty of getting sulfur during the war had a depressing effect on the chemical-pulp industry, although some of the plants managed to get along with Norwegian pyrites. The pre-war importation of sulfur was about 40,000 tons a year, the principal source of supply being Italy. Considerable quantities have since been obtained from the United States.

Some 350,000 tons of paper and cardboard are produced in Sweden annually, and the newspapers of Europe are pretty much dependent upon this source of supply. The finest grades of paper are imported.

Wood-distillation products are an important factor in any consideration of the Swedish chemical industry. In the order of quantity produced, these products are tar and tar oil, rosin, turpentine, acetate of lime, pitch and pitch oil, methanol, formalin, wood oil, and creosote. Charcoal is still used extensively in iron smelting, but most of it is made in kilns rather than ovens.

Rapid strides have recently been made in the manufacture of spirits from the residual lye of the sulfite-pulp factories. It is estimated that the potential yield from the residue now available is not less than 36,000,000 liters of 100 per cent spirits a year. The actual production is said to be about 12,000,000 liters.

PRODUCTION OF METALS

The Swedish iron and steel industry is not in the front rank in point of quantity produced, but for quality its reputation is unexcelled. The ores are of excellent quality, and the smelting, formerly with charcoal and latterly largely with electric current, has given to the world a wonderfully fine iron. The increasing use of electricity in the manufacture of steel has also set a high standard in that line. Swedish steel is liked in this country for safety-razor blades, and Swedish ball bearings find their way into all countries. The production of iron ore totals some 7,000,000 tons a year, and makes up more than 95 per cent of the metalliferous ores mined.

The production of ferro-alloys is important, and has kept pace with the growth of the steel industry.

A war development was the revival of copper production, which once was an important feature of Swedish industry. It is not expected that the industry will grow to large proportions, but it is likely that the success of electrolytic refining of copper will insure the continuance of a domestic supply of refined copper.

ELECTROCHEMICAL INDUSTRY

Hydroelectric power has not been developed in Sweden on quite so grand a scale as in Norway, nor is it used in the same proportions for the various industries, but it is a mighty factor in the country's prosperity. As in Norway, the development has taken place to offset the lack of coal. In the electrochemical industry, the chief use of current is for the manufacture of pig iron, ferro-alloys, and calcium carbide. The fixation of atmospheric nitrogen is comparatively unimportant when the extent of this industry in Norway is recalled.

Arranged in the order of power used, the various Swedish electrochemical industries are as follows: Pig iron, 90,000 horsepower; ferro-alloys, 60,000 horsepower; calcium carbide, 40,000 horsepower; atmospheric nitrogen, 16,000 horsepower; steel, 10,000 horsepower; caustic soda and bleaching powder, 3,000 horsepower; potash salts, 2,700 horsepower; graphite, 2,000 horsepower; phosphorus, 1,500 horsepower. The figures are estimates for 1918.

As in other countries where waterpower is available, the development of hydroelectric plants was greatly stimulated by the war.

FERTILIZERS

Although the agricultural products of Sweden do not enter largely into international trade, the fact remains that half the population is engaged in farming, and fertilizers are an important item in the Swedish chemical market.

Before the war there were heavy importations of the following artificial fertilizers, in the order of quantity: potash salts, from Germany; raw phosphate, from the United States, England, Germany, Australia, and Tunis; sodium nitrate, originating in Chile, but imported from Germany; Thomas phosphate and slag, from England and Belgium; and superphosphate, from Belgium and the Netherlands. As Sweden was in a position to trade with Germany during the war, it was natural that the imports of potash should increase after hostilities commenced. It was just as natural that the imports of phosphate should fall to a low figure, that the imports of sodium nitrate should be cut in half, and that outside supplies of superphosphate and Thomas phosphate should be cut off entirely. Calcium nitrate has been imported from Norway since the war started.

The domestic manufacture of fertilizers cannot meet the home demand, but it has grown to great proportions. With normal supplies of phosphate there is a thriving export business in superphosphate, Norwegian and Swedish pyrites being used for the manufacture of the necessary sulfuric acid. The imports of superphosphate mentioned above form only a small part of the consumption. Cyanamide is a product of the electrochemical industry. Swedish iron ores are rich in apatite and yield a rich Thomas slag. Animal waste and bone meal are important domestic items, and the production of fish guano is in normal times a feature of the herring industry, although it practically disappeared during the war.

There was the same shortage of fertilizers during the war as in other countries, as shown by the production and trade statistics included in this article.

PRODUCTION OF MATCHES

Judging from the latest production figures available, the manufacture of Swedish safety matches was stimulated by the war, as the output was increased from 73,000,000 lbs. in 1913 to 114,000,000 lbs. in 1917. It does not appear from the statistics, however, that all of the increased production went into foreign trade, for the export returns are 61,000,000 lbs. for 1913; 85,000,000 lbs. for 1917; 63,000,000 lbs. for 1918; and 61,000,000 lbs. for 1919. Later production figures would probably show a falling output.

Swedish safety matches need no introduction to the outside world, as they were standard for years before the war. They failed to reach the United States during the war, and the character of the substitutes offered, especially by Japan, is still well remembered. It is also common knowledge that the American product was improved, until it is now generally accepted as quite satisfactory. The efforts of the Swedish manufacturers to regain the lost ground will be watched with interest.

The Swedish industry has unlimited supplies of match wood to draw from, both at home and in Finland, most of the material in the past coming from the latter country. The home supplies are in rather inaccessible parts of the country, but these have been opened up to some extent since communication with Finland became uncertain. Phosphorus is now produced by an electric smelting method that promises to supply the needs of the match industry. Potassium chlorate has been manufactured in Sweden for many years, and the production is not only sufficient for the match industry, but supplies a surplus for export. Potassium chloride, the raw material, is imported from Germany. Machinery for making and packing matches has been developed to a state of extraordinary efficiency.

STATISTICS OF PRODUCTION

A comparison of production statistics for 1913 and 1917 will reveal the proportions of the Swedish chemical industry and the effect of war conditions on output—the stimulating effect of war prices, and the depressing effect of decreased imports of raw materials. The table has been compiled from official figures published by the Swedish Department of Commerce, of the Board of Trade.

PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC.:			
Acids:			
Acetic	1,610,675	977,488	973,004
Nitric	1,188,380	4,205,442	3,051,519
Hydrochloric	5,434,167	2,362,958	3,030,077
Phosphoric	1,222,216	963,949	662,242
Sulfuric	185,040,128	168,127,363	121,750,874
Aluminium compounds (hydrate, sulfate, etc.)	12,730,118	38,744,978	36,426,976
Ammonia, liquid	8,080,382	13,081,175	8,945,455
Ammonium:			
Caustic	1,675,480	2,526,036	2,575,142
Nitrate	1,431,408	1,508,193	1,420,083
Sulfate	3,035,014	2,954,827	2,874,902
Calcium carbide	70,441,652	80,153,528	76,437,825
Carborundum	....	110,231	....
Chloride of lime	1,188,064	3,408,346	3,660,195
Chrome alum	....	....	15,400
Coal tar and products:			
Asphaltic, mastic, and similar preparations	15,738,869	14,884,316	9,649,873
Benzene products	(1)	1,506,432	1,636,057
Coal tar	28,728,900	35,269,646	27,006,529
Other coal-tar products	2,552,953	4,637,747	3,295,429
Copper:			
Scales and oxide	....	192,212	154,227
Sulfate	942,586	2,795,351	2,106,517
Cosmetics and toilet preparations	$801,610	$980,212	$1,223,650
Fertilizers	587,339,974	456,088,200	338,027,823
Animal waste	72,294,571	72,015,148	85,365,501
Bone meal	12,832,516	17,714,720	11,812,889
Fish guano	1,287,543	223,119	31,195
Nitrogen carbide	40,460,315	58,222,143	38,830,208
Superphosphate	406,221,652	270,652,594	165,280,410
Thomas phosphate	40.463,419	29,227,776	26,836,449
Other	13,779,958	8,032,700	9,871,171
Ferrous sulfate	706,030	616,170	322,470
Glauber's salts	12,397,112	9,196,141	11,232,681
Glycerol:			
Raw	321,500	1,284,065	648,322
Purified	1,071,898	1,327,919	369,395
Nitrobenzene	....	263,126	251,214
Perfumes	$176,755	$251,104	$410,508
Phosphorus	....	....	222,005
Potash:			
Caustic	310,356	507,063	282,716
Chlorates and perchlorates	7,955,011	9,289,935	10,929,096
Nitrate	....	400,381	373,862
Yellow prussiate	236,708	....	....

[1] Not given separately.

PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC. (*Concluded*):			
Soda:			
Bisulfate	....	5,869,385	5,746,511
Caustic	360,425	1,353,171	1,629,029
Crystals	28,418,289	14,965,911	8,122,724
Tanning materials, vegetable	6,261,127	13,182,737	14,191,426
Water glass	2,956,487	2,741,329	1,943,317
GUMS AND RESINS:			
Dextrin and preparations	796,149	1,642,834	1,177,564
Elastic glue for printing cylinders	....	518,086	299,659
Liquid glue and gum	940,428	1,862,004	2,610,855
Marine glue and gelatin	4,207,682	5,430,924	4,500,367
Rosin	137,789	191,114	726,480
Rosin glue	2,764,407	2,002,397	496,327
WOOD-DISTILLATION PRODUCTS:			
Acetate of lime	....	2,449,395	1,799,532
Acetone	....	60,252	108,778
Creosote	....	54,509	15,609
Formalin	278,658	408,651	676,111
Methanol	1,161,289	1,304,559	989,212
Pitch and pitch oil	397,848	727,126	1,763,559
Rosin, liquid	1,747,853	5,313,857	6,619,383
Tar and tar oil	14,553,776	17,177,663	14,639,054
Turpentine oil	1,387,446	4,267,637	4,535,608
Wood oil	376,488	455,863	430,752
Other (including creosote oil)	....	726,076	1,492,346
	Metric Tons	Metric Tons	Metric Tons
ORES, ETC.:			
Copper	5,458	13,895	13,579
Graphite	250	320	211
Gypsum	....	910	....
Iron	7,479,393	6,988,740	6,220,338
Manganese	4,001	8,894	19,873
Manganese, pulverized	73	154	154
Molybdenum	....	3	137
Nickel	....	3,561	4,991
Silver-lead	3,222	3,707	3,709
Sulfur pyrites and manganese pyrites	34,319[1]	97,848	142,366
Zinc	50,752	60,700	51,312
Zincblende	33,853	48,221	9,727
	Pounds	Pounds	Pounds
PAINTS AND VARNISHES:			
Bone-black	132,277	106,042	192,067
Bronze paint	40,371	38,308	35,949
Butter and cheese coloring	166,109	185,519	43,398
Earth colors	1,766,317	2,390,438	1,990,703
Inks, printing	1,916,152	1,061,591	1,680,826
Lacquer and enamels	....	751,743	428,343
Lampblack	1,613,800	1,480,322	1,053,810
Ocher, red	4,549,739	4,479,887	2,713,618
Oil paints	1,629,593	2,770,132	1,788,833
Putty paint	685,159	711,535	513,754
Varnishes	3,438,424	3,819,392	3,422,306
Other colors	695,889	1,870,876	221,529
Other similar preparations	$24,553	$70,280	$55,172
TOTAL, paints and varnishes	$927,707	$2,128,364	$3,102,177
OILS, FATS, AND WAXES:			
Animal oils	150,338	877,677	274,286
Bone fat	1,805,566	1,729,193	2,391,224
Candles	5,351,743	2,943,901	951,085
Greases	5,824,171	5,997,312	2,304,174
Leather oils and greases	640,560	1,243,857	451,798
Linseed oil	19,294,931	20,815,356	....
Linseed-oil substitute	....	691,903	1,735,302
Machine and axle grease	2,401,006	2,177,852	1,932,199
Oilcake:			
Linseed cake and meal	41,466,995	44,603,263	....
Rapeseed cake	1,118,846	678,406	....
Olein and other fatty acids	1,053,111	2,278,389	2,704,395
Oleomargarine	1,328,223	1,187,182	....
Soap and similar products	63,378,621	73,272,959	42,509,212
Soft soap	44,453,715	55,288,907	20,029,208
Soft-soap substitute	....	....	5,070,358
Toilet soap	6,694,373	5,756,072	5,260,130
Other soap	4,562,510	3,797,586	4,550,253
Washing and soap powder	7,668,023	8,430,394	7,599,263
Stearin	2,488,234	2,246,112	975,614
Stearin wax	89,100	154,573	215,017
Tallow:			
"Premier jus"	613,355	1,557,008	99,722
Compressed	659,072	589,152	24,701
Dyretalg	288,975	633,179	195,330
Turnip and rapeseed oils	697,102	433,702	15,432
Other oils and fats	603,747	3,047,209	2,823,423
	Metric Tons	Metric Tons	Metric Tons
MISCELLANEOUS MANUFACTURES:			
Chalk	19,037	19,022	15,435
	Pounds	Pounds	Pounds
Explosives:			
Dynamite and other explosives containing nitroglycerin	4,676,460	5,240,654	5,532,828
Explosives not containing nitroglycerin	186,458	145,520	371,827
Fireworks	$4,824	$8,950	$9,385
Fuses	260,322	410,677	250,313
Guncotton:			
Compressed	61,132	100,853	56,970
Not compressed	635,917	1,450,463	1,066,400
Nitrated	....	518,086	299,659
Powder:			
Black	724,011	530,079	478,657
Smokeless	541,724	1,302,700	1,066,076

[1] Sulfur pyrites only.

PRODUCTION OF CHEMICALS AND ALLIED PRODUCTS (*Concluded*)

	1913 Pounds	1916 Pounds	1917 Pounds
MISCELLANEOUS MANUFACTURES (*Concluded*):			
Gases:			
Acetylene[1]	176,577	322,876	395,082
Carbonic acid	1,999,749	1,956,020	1,919,911
Hydrogen	410	5,952	4,702
Oxygen	393,338	967,243	1,367,880
Other	2,538	24,456	49,622
	Cubic Feet	Cubic Feet	Cubic Feet
Gas works:			
Acetylene gas	1,149,718	164,351	94,818
Coal gas	3,038,032,803	3,641,093,300	3,067,932,707
Water gas	55,949,736	178,699,081	249,589,335
	Pounds	Pounds	Pounds
Glass and manufactures:			
Bottles	66,675,066	68,901,531	44,455,756
Flasks and jars for medicines	6,041,556	7,558,724	9,392,998
Window glass	21,410,928	21,588,255	17,043,580
Other glass manufactures	$1,548,740	$2,645,616	$3,425,974
Insulating material	918,536	1,709,358	1,682,581
Mantles, gas and electric	30,776	75,727	65,222
Matches:			
Safety	72,782,851	117,873,166	114,238,116
Other	16,858,807	8,726,715	1,715,723
Paper and pulp:			
Cardboard	107,124,750	173,281,355	120,243,352
Paper	626,918,053	729,480,953	615,313,118
News print	204,552,662	267,615,805	244,104,797
	Metric Tons	Metric Tons	Metric Tons
Pulp	1,186,577	1,324,458	1,023,661
	Pounds	Pounds	Pounds
Sealing wax	122,544	152,165	151,689
Shoe polishes and finishes	1,550,154	4,980,741	4,919,637
Sugar:			
Beet pulp	891,337,572	949,515,408	998,907,069
Cut sugar	16,163,950	16,391,092	14,723,791
Molasses	44,757,155	60,882,120	57,737,621
Raw sugar	290,924,786	280,762,641	302,904,126
Refined sugar	297,072,770	314,957,660	256,608,238
Sirup	8,094,771	30,379,045	27,634,827

[1] See also item under "Gas works."

STATISTICS OF IMPORTS

Swedish trade statistics are published monthly and annually. The latest are to be found in the monthly returns, but the list of chemicals is a short one and the countries of origin are not shown. However, to give an idea of tendencies during the first year of peace, a table has been compiled from these returns showing

SUMMARY OF IMPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1918 Pounds	1919 Pounds
CHEMICALS, DRUGS, ETC.:			
Caustic potash and soda	11,669,137	1,779,064	11,599,706
Chloride of lime	....	2,438,711	11,284,073
Fertilizers:			
Phosphate	243,498,202	80,924,806	152,823,478
Thomas phosphate and slag	42,424,088	....	....
Glycerol, crude and refined	736,969	87,681	1,255,502
Phosphorus, white and red	....	119,996	84,546
Potash salts	176,925,982	232,385,613	275,361,721
Salt, table	53,615,036	50,690,859	31,581,354
Sodium:			
Carbonate and bicarbonate	40,206,516	5,323,997	31,343,438
Nitrate	74,717,450	14,909,492	51,174,253
Sulfate and bisulfate	70,008,208	80,982,088	29,706,451
Sulfur	84,198,112	....	43,798,438
	Metric Tons	Metric Tons	Metric Tons
Sulfur pyrites	131,875	109,652	71,304
	Pounds	Pounds	Pounds
Tanning extracts, vegetable	19,710,861	690,955	28,582,491
COLORS AND DYES:			
Coal-tar colors	2,149,536	927,907	1,484,882
Varnish	1,342,679	232,184	3,626,763
Zinc white, white sulfide of zinc, and white baryta	11,314,192	1,484,882	5,776,334
GUMS AND RESINS:			
Caoutchouc, all kinds	2,348,785	1,119,375	4,530,237
Resins, including turpentine and other native balsams	15,657,259	408,151	9,777,141
OILS, FATS, AND WAXES:			
Mineral oils:			
Benzine and gasoline	(1)	3,058,029	52,695,553
Illuminating oil, purified	265,316,714	43,275,745	163,114,802
Lubricating oil	(1)	25,568,369	51,248,553
Other	130,675,963	17,301,291	91,463,911
Oilcake	346,703,690	14,160,785	151,308,131
Olein and other fatty acids, n. e. s.	1,852,717	15,265	1,286,770
Oleomargarine	1,265,831	....	4,172,721
Paraffin, raw or refined	7,185,792	2,890,522	5,956,324
Tallow	8,293,123	2,489	8,475,276
Turpentine oil	1,099,661	2,438	827,492
Vegetable fixed oils	61,909,522	1,802,316	91,444,740
Whale oil	3,361,219	131,401	986,459
SUGAR	4,683,073	25,464,605	20,804,546

[1] Not stated separately.

the trade in chemicals and allied products in summary form for the years 1913, 1918, and 1919. With this table and the detailed table for 1913, 1916, and 1917 compiled from the annual returns, it will be possible to study the extent and character of the Swedish market for imported chemicals, and the effect the war has had upon it. The tables are based upon publications issued by the Swedish Department of Commerce, of the Board of Trade.

The following table, showing the import trade in detail and by countries, is based upon the latest annual statistics:

Imports of Chemicals and Allied Products

	1913 Pounds	1916 Pounds	1917 Pounds
Chemicals, Drugs, Etc.:			
Acetate of lime	198,171	386	28,259
Acids:			
Boric	264,777	159,233	102,579
Germany	178,969	....	....
United Kingdom	75,978	124,186	100,200
Citric and tartaric	203,185	306,881	47,062
France	34,502	126,060	11,102
Germany	106,005	....	....
Italy	....	49,121	....
United Kingdom	31,676	100,617	....
Formic and lactic	251,605	427,234	24,881
Hydrochloric	3,183,470	1,572,775	87,468
Germany	3,141,622	1,471,299	....
Hydrofluoric acid and fluoride of ammonium	59,417	147,452	13,272
Germany	58,570	147,452	....
Nitric	191,848	6,017,951	5,009,204
Denmark	36,528	6,015,414	5,009,204
Germany	155,320	....	....
Oxalic	169,203	1,308,415	890,429
Germany	158,078	1,308,399	890,429
Phosphoric	8,391	2,945	357
Salicylic	19,141	51,176	130
Sulfuric (including sulfurous anhydride)	2,455,733	1,305	115
Germany	1,540,751	....	....
Netherlands	863,207	....	....
Tungstic	906	2,280	....
Albumin	10,721	26,398	119
Alum	99,358	213,855	530,196
Aluminium:			
Pure and hydrate	626,084	32,163	10,873
Sulfate	4,798,925	502,076	2,783,472
Germany	....	303,530	1,754,833
United Kingdom	2,604,402	....	256,938
United States	....	....	672,218
Ammonium:			
Carbonate	367,369	620,641	333,980
Germany	....	27,355	199,236
United Kingdom	344,596	396,821	55,354
Caustic	161,303	16,193	2,150
Nitrate	137,635	327,162	793,519
Germany	79,269	....	....
Norway	57,836	327,162	793,519
Sal ammoniac	429,315	645,033	2,328
Sulfate	83,352	3,091,191	686,394
United Kingdom	....	3,090,741	686,308
Ammonium, potassium, and sodium phosphate	50,788	125,152	35
Germany	49,306	....	....
United States	....	99,880	....
Arsenic, white	80,136	355,149	80,209
Germany	....	355,149	80,209
Barium protoxide (baryta) and barium peroxide (gray powder)	....	148,834	55
Germany	....	148,834	....
Borax	1,036,219	1,099,707	388,756
Denmark	....	69,875	....
Germany	548,843	1,746	....
United Kingdom	483,542	535,342	186,211
United States	....	471,403	202,545
Bromine, potassium bromide, etc.	24,716	39,225	19,074
Germany	24,341	34,540	19,050
Calcium and barium carbide	5,225	18	8,483
Calcium, barium, and aluminium chloride	653,831	2,351,281	513,904
Germany	322,367	2,189,999	468,696
Carbon disulfide and chloride of sulfur	81,192	41,301	24
Carborundum	86,401	248,132	454,893
Denmark	26,403	....	....
Germany	50,014	....	....
Norway	....	200,288	409,577
Switzerland	....	....	43,755
United States	....	39,392	1,561
Casein	459,137	865,361	22,046
Denmark	....	....	22,046
France	244,826	631,404	....
Germany	113,822	....	....
United Kingdom	....	163,012	....
Celluloid	375,181	301,907	201,758
Chemical preparations, n. e. s.	1,438,890	2,037,095	846,383
Germany	1,068,274	1,858,768	718,833
Chemicals, Drugs, Etc. (Continued):			
Chloride of lime	16,266,542	8,474,650	4,812,742
Belgium	853,270	....	....
Denmark	51,141	452,583	....
Germany	4,485,293	2,589,613	1,558,679
Norway	....	851,438	255,145
United Kingdom	10,876,837	1,323,069	....
United States	....	3,109,748	2,796,826
Chrome acetate and iron acetate	8,717	2,802	220
Chrome alum	453,039	43,283	44,077
Chromium sulfate	1,627	36,354	33
Coal tar and products:			
Benzene oils	461,773	1,940,127	206,311
Germany	218,403	1,832,669	184,333
Norway	84,471	....	....
United Kingdom	120,803	....	....
United States	....	107,458	....
Carbolic acid, cresol, and creosote oil	8,225,762	4,713,924	113,559[1]
Germany	3,057,200	36,369	....
United Kingdom	5,136,797	4,667,440	....
Carbolineum	306,054	2,425	492
Coal tar	14,723,234	4,852,424	2,439,397
Denmark	7,616,168	....	220,460
Germany	4,487,792	....	....
Norway	1,066,266	1,030,298	589,565
United Kingdom	1,552,953	3,568,540	1,629,371
Naphthalene	216,399	709,226	618,635
Germany	190,341	675,216	605,522
Other coal-tar products	584,995	291,309	55,071
United Kingdom	356,162	138,960	....
United States	....	125,012	....
Copper:			
Oxide	7,211	231	....
Sulfate	145,062	111,622	1,008
Drugs and toilet preparations:			
Hair dye	7,319	7,681	6,475
Perfumery and cosmetics	58,034	63,554	67,833
Salicylic preparations	47,291	99,826	15,009
Germany	44,597	93,909	14,647
Tartar emetic	27,262	5,057	450
Toilet water	42,485	32,926	9,081
Tooth powder and paste	3,287	3,591	2,277
Other drugs	261,772	371,308	126,011
British South Africa	....	3,552	23,874
Denmark	20,456	15,562	11,883
Germany	197,400	196,187	35,207
Netherlands	....	6,515	22,912
Russia, European	....	43,089	....
United Kingdom	18,336	56,431	15,582
United States	....	21,215	....
Fertilizers:			
Calcium nitrate	....	2,280,084	3,159,158
Norway	....	2,280,084	3,159,158
Nitrogen carbide	110	37	....
Phosphate, raw	271,717,082	189,436,304[2]	3,863,782
Australia	37,116,513	....	....
Germany	49,265,777	....	....
Tunis	22,300,836	19,764,695	....
United Kingdom	73,915,963	....	....
United States	76,106,516	131,470,331[2]	....
West Indies	....	14,273,934	3,863,782
Potash salts:			
37 per cent potash	63,110,907	106,170,904	32,354,622
Germany	63,110,691	106,170,904	32,354,622
20 per cent potash	61,799,524	120,812,090	59,352,465
Germany	61,796,878	120,812,090	59,352,465
12 per cent potash	51,725,248	5,516,150	....
Germany	51,607,697	5,516,150	....
Other	1,713	176,370	419
Sodium nitrate	74,718,261	80,159,488	37,848,293
Chile	232,524	70,196,432	....
Germany	72,873,155	....	....
United States	....	....	35,252,615
Superphosphate	7,188,092	3,261	....
Belgium	3,985,223	....	....
Netherlands	2,830,786	....	....
Thomas phosphate and slag	46,670,839	3,406,141	....
Belgium	14,282,845	....	....
Germany	703,715	3,406,141	....
United Kingdom	30,517,817	....	....
Formalin	19,279	48,627	112
Glycerol:			
Crude	43,512	585,632	668,000
Denmark	....	462,990	414,710
Finland	33,658	....	....
Norway	....	122,642	67,547
United States	....	....	185,743
Refined	694,925	39,804	778
Germany	206,026	....	....
Netherlands	357,119	39,804	....
United Kingdom	113,089	....	....
Hydrogen peroxide	153,814	270,992	94,177
Germany	....	268,836	94,177
Insect powder	18,686	44,198	29,943
Iodine, potassium iodide, etc.	11,574	13,400	1,680
Germany	11,570	12,749	....
Iron:			
Oxyhydrate	9,163,781	5,665,433	1,938,712[3]
Germany	7,909,374	1,291,578	....
Netherlands	1,111,130	3,723,481	....
Sulfate	1,660,495	231,302	143,360
Germany	1,004,062	....	....

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[1] Not given by countries.

[2] Including 11,460,784 lbs. of "apatit."

[3] Not given by countries in 1917.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC. (*Continued*):			
Lead:			
Nitrate	1,678	430	137
Oxide and peroxide	719,917	1,492,957	90,407
Germany	438,636	496,232	....
United Kingdom	164,659	881,999	....
Sugar of lead and lead vinegar	145,454	66,983	27,928
Magnesia, calcined or carbonate	75,111	379,980	336,807
Magnesium:			
Chloride	1,759,456	7,215,702	1,528,163
Germany	1,659,163	7,180,621	1,527,259
Sulfate	1,612,458	3,870,492	968,610
Germany	1,619,147	3,825,770	968,610
Nickel oxide and sulfate	71,231[1]	108,866	89,852
Nitrate of silver	1,215	2,449	432
Nitrobenzene	142,832	2,216	....
Phosphorus	203,899	228,677	46,709
United Kingdom	184,218	222,285	37,018
Phosphorus sesquisulfide and hydride	70,140	114,861	....
United Kingdom	69,898	114,861	....
Potash	3,124,528	6,020,191	3,920,782
Germany	2,761,228	5,910,621	3,880,752
Potash, yellow prussiate of	25,142	253,256	363,723
Germany	....	250,189	363,692
Potassium:			
Chloride	4,586,802	9,768,016	4,067,623
Germany	4,584,574	9,682,029	4,067,616
Nitrate	661,836	7,687	21,881
Germany	641,378	....	....
Sulfate	125,465	308,347	37,101
Germany	125,443	308,347	....
Potassium and sodium:			
Arsenite	77	1,437	3,748
Caustic:			
Solid	4,282,697	6,997,643	1,466,250
Germany	573,718	6,138,301	1,256,591
Netherlands	104,845	186,870	....
United Kingdom	3,469,663	116,468	....
United States	....	506,812	176,268
Liquid	7,257,068	12,112,326	1,705,421
Germany	7,173,445	12,077,640	1,623,266
Chlorate	558,740[2]	399	7
Chromate	308,233	220,537	260,650
Germany	68,323	1,373	....
United Kingdom	219,012	20,849	12,070
United States	....	173,250	248,580
Cyanide	16,793	28,892	31,976
Potassium, sodium and calcium sulfide	1,273,679	3,164,497	610,244
Germany	654,969	3,032,452	565,907
United Kingdom	523,058	....	....
Rennet	256,268	162,494	61,291
Saccharin	....	1,385	220
Salt, common	54,954,351	61,889,071	47,797,440
Germany	39,338,635	48,057,912	47,355,920
United Kingdom	12,040,373	11,515,241	....
Salts:			
Formaldehydesulfoxylic acid	17,205	9,572	5,234
Gold, platinum, and radium salts	95	161	49
Stannate, stannic chloride and putty powder	125,624	65,733	38,036
Soda	40,726,788	32,997,872	8,420,134
Germany	32,949,191	17,424,528	5,491,199
United Kingdom	4,682,840	4,060,383	433,405
United States	....	10,403,531	2,386,420
Sodium:			
Acetate	68,881	584	445
Sulfate and bisulfate	69,975,599	121,152,066	102,081,969
Belgium	2,250,368	....	....
Germany	11,481,468	78,800,963	98,525,118
Netherlands	....	18,766,530	3,306,250
United Kingdom	54,026,473	22,233,088	....
Sulfite	649,885	2,898,465	682,600
Germany	434,364	2,815,946	646,695
Sulfur	87,557,545	59,268,010	32,195,890
Germany	6,476,439	....	....
Italy	49,181,777	43,863,181	....
United Kingdom	23,340,804	8,328,587	11,199
United States	8,536,780	7,076,238	32,184,682
Tanning materials:			
Catechu	452,728	184,066	4,220
Germany	439,456	....	....
United Kingdom	....	178,705	....
Oak bark	364,094	....	50,300
Quebracho	10,777,774	9,327,041	969,328
Argentina	696,169	6,992,621	611,377
Belgium	664,486	....	....
France	709,469	....	....
Germany	6,315,498	58,360	....
United Kingdom	2,233,377	50,600	....
United States	....	1,333,459	157,951
Tannic acid	189,443	33,503	2,046
Other	8,407,557	1,428,506	52,902[3]
France	3,387,095	....	....
Germany	2,740,108	303,800	....
United Kingdom	620,491	496,233	....
United States	....	476,632	....

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC. (*Concluded*):			
Tartar	56,732	270,999	68,965
Denmark	....	22,399	22,046
France	36,332	49,926	....
Italy	....	66,529	46,297
Spain	....	93,053	....
United Kingdom	....	23,089	622
United States	....	10,935	....
Thorium nitrate	4,799	12,154	13,726
Water glass	1,653,160	2,716,593	1,498,440
Germany	1,120,826	2,239,352	1,367,701
Norway	....	186,105	120,798
United Kingdom	....	236,078	....
Zinc sulfate and chloride	314,077	503,346	139,614
Germany	....	494,958	139,614
COLORS AND DYES:			
Bone-black	243,725	168,839	27,212
Germany	....	144,398	....
Bronze and color leaf	5,454	8,087	6,975
Germany	4,394	7,635	6,766
Bronze powder	22,661	14,339	26,451
Butter and cheese coloring	21,118	12,489	4,561
Chalk:			
Ground, washed, or precipitated	3,321,223	1,372,802	1,381,850
Denmark	2,477,518	....	....
Germany	706,995	588,335	308,595
For schools, and French chalk	88,654	97,082	82,309
Colors for typographic, lithographic, and plate printing	58,220	105,888	49,348
Germany	47,633	64,833	34,469
Colors prepared with oil:			
For ships' bottoms	415,840	335,464	83,934
Germany	85,608	45,051	....
Norway	....	....	20,968
United Kingdom	282,053	266,668	....
United States	....	....	35,783
Other	135,221	177,763	88,390
Dyes:			
Alizarin dyes	136,596	78,143	54,494
Germany	128,940	77,978	54,494
Aniline and other tar dyes	2,049,538	1,768,552	1,835,070
Denmark	20,741	18,607	....
Germany	1,873,519	1,728,450	....
Netherlands	50,115	....	....
Switzerland	87,096	18,062	....
Cochineal	1,312	1,360	99
Dyestuffs:			
Aniline (aniline oil)	52,523	30,190	22,641
Germany	49,886	18,735	11,442
United States	....	11,455	11,199
Dyewoods	551,170	198,859	2,303,673
Whole or in pieces	....	2,183	2,255,306
Ground	....	....	....
Brazil wood	171,397	23,677	1,102
Other	379,773	65,164	2,152
Germany	357,646	64,998	....
Extracts	232,940	65,821	45,029
Other vegetable dyestuffs	13,397	42,015	84
Indigo	191,399	84,994	68,091
Natural	1,345	359	....
Synthetic	115,376	40,917	42,935
Germany	110,104	38,036	42,935
Other indigo coloring matters	74,679	43,717	25,157
Germany	74,679	39,707	....
Earth colors	3,822,082	4,889,477	2,728,786
France	953,587	1,307,121	....
Germany	2,536,275	3,440,638	2,560,612
Ink, ink powder, and India ink	43,740	48,810	32,624
Germany	24,928	33,010	....
Ink, printer's	187,702	119,562	57,626
Denmark	25,095	11,790	26,131
Germany	155,982	100,043	28,424
Lampblack	293,046	705,763	308,340
Germany	212,418	594,129	299,662
Mineral colors	20,442,170	39,169,627	13,362,960
Cobalt oxide	22,811	10,538	14,423
Germany	14,156	....	9,367
United Kingdom	8,060	6,367	....
Red ocher	1,432,068	1,341,815	477,254
Germany	950,662	827,364	349,719
United Kingdom	463,473	514,451	127,535
Red lead	2,589,373	4,629,058	276,118
Germany	949,474	2,107,601	....
Netherlands	300,128	148,812	....
United Kingdom	1,234,256	2,370,022	....
United States	....	2,646	144,169
White lead	1,341,310	2,172,587	4,965
Germany	809,008	1,089,765	....
Netherlands	390,851	485,017	....
United Kingdom	126,332	350,755	....
United States	....	220,462	....
White sulfide of zinc and white baryta	2,681,499	8,642,199	2,544,368
Belgium	266,462	....	....
Denmark	....	....	151,171
Germany	1,460,304	8,093,907	2,393,197
Netherlands	811,369	448,524	....
United Kingdom	104,087	....	....
Zinc white	8,707,802	16,185,980	7,303,080
Belgium	206,540	51,809	....
Denmark	69,931	337,969	....
Germany	5,810,705	14,387,472	5,915,839
Netherlands	2,424,277	1,199,050	1,364,452
United Kingdom	120,505	....	....
United States	....	204,082	....

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[1] All sulfate.
[2] All potassium chlorate.
[3] Not given by countries.

IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
COLORS AND DYES (*Concluded*):			
Mineral Colors (*Concluded*):			
Other	3,667,283	6,187,418	2,742,775
Belgium	326,987	....	....
Germany	2,597,210	5,834,909	2,636,481
Netherlands	368,348	170,519	....
United Kingdom	322,713	122,509	63,220
Pastilles and black chalk	48,744	88,905	52,223
Germany	39,427	80,221	45,185
Tar colors, with addition of solvents	109,730	136,956	60,305
Germany	56,581	80,825	53,345
Varnish:			
Spirit	30,556	33,843	3,082
Oil	235,709	113,230	247,546
Finland	....	....	165,089
Germany	98,896	....	....
Netherlands	109,386	....	....
United Kingdom	....	79,725	15,964
United States	....	....	51,008
Other	1,090,402	1,012,692	430,137
Germany	344,965	96,334	....
Netherlands	212,614	49,557	....
United Kingdom	249,484	293,152	29,573
United States	257,574	556,002	370,975
OILS, FATS, AND WAXES:			
Acetone and acetone oil	141,593	182,944	29,077
Germany	140,246	32,635	....
United States	....	144,679	29,046
Animal fat	471,637	1,112,809	405,675
Denmark	....	....	396,718
Norway	435,711	....	....
United Kingdom	....	1,082,893	....
Animal oils	3,641,847	511,518	675,340
Denmark	1,125,234	108,398	527,049
Norway	1,623,002	288,016	77,712
Bitter-almond oil	15,016	4,015	1,462
Ceresin	146,736	221,340	1,213
Germany	135,373	92,836	....
United Kingdom	....	55,917	....
United States	....	72,364	....
Collodion	7,321	2,112	3,779
Degras (tanners' fat)	294,885	220,420	....
Germany	280,086	47,577	....
Norway	....	48,197	....
United Kingdom	....	74,630	....
United States	....	50,016	....
Disinfectants containing soap	49,066	5,975	4,786
Greases:			
Machine and wagon grease	1,832,558	1,254,400	223,630
Belgium	426,976	....	....
Denmark	....	152,349	....
Germany	890,438	....	....
United Kingdom	271,549	84,809	....
United States	....	1,014,896	127,216
Other	894,433	612,537	379,689
Belgium	219,433	....	....
Denmark	....	203,886	....
Germany	419,452	....	....
United Kingdom	176,536	287,925	135,717
United States	....	118,594	222,332
Lanolin	188,780	103,043	33,420
Germany	160,252	....	....
United Kingdom	....	95,322	29,107
Lubricating oils (mixed fatty and mineral oils)	2,462,878	1,567,016	1,229,413
Finland	....	....	402,556
Germany	1,005,474	....	....
United Kingdom	866,862	95,164	....
United States	246,256	1,397,128	751,506
Mineral oils:			
Crude	37,167,287	23,581,010	8,113,219
Austria	27,867,729	....	204,190
United Kingdom	502,362	2,244,530	....
United States	3,610,745	21,323,497	7,894,371
Refined:			
Benzine and gasoline	33,981,235	32,334,174	7,447,485
Netherlands	14,403,386	....	....
United Kingdom	5,110,596	1,985,998	....
United States	12,782,026	30,282,037	7,419,039
Illuminating	265,601,092	239,450,380	82,346,019
Denmark	38,168,575	17,046,600	....
United States	207,951,263	222,262,172	82,245,301
Lubricating	49,323,981	50,978,809	15,227,069
Denmark	1,128,114	5,962,297	635,311
Germany	10,932,215	....	....
Russia, European	25,423,939	....	2,227,839
United States	10,332,103	44,904,327	11,093,007
Other	10,601,092	12,767,967	83,288
Austria	1,643,759	....	....
Denmark	1,873,659	....	....
Netherlands	2,742,295	....	....
United Kingdom	3,475,058	253,802	....
United States	....	12,483,883	....
Olein	1,831,191	3,213,998	1,113,991
Belgium	945,612	....	....
Netherlands	436,401	238,088	....
United Kingdom	....	2,333,838	572,883
United States	....	577,934	362,020
Oleomargarine	1,289,969	3,086,802	1,111
France	599,733	519,653	....
Norway	66,310	2,473,178	....
Oilcake:			
Cottonseed	20,911,601	92,112,205	66,413,156
Argentina	....	2,735,909	....
Denmark	3,178,835	....	....
Germany	3,989,041	....	....
Russia, European	2,624,570	....	....
United Kingdom	1,573,899	....	....
United States	9,434,857	88,811,775	66,413,156
OILS, FATS, AND WAXES (*Continued*):			
Oilcake (*Concluded*):			
Hempseed	959,687	....	....
Germany	649,235	....	....
Russia, European	277,244	....	....
Linseed	9,609,992	....	....
Denmark	876,340	....	....
Germany	1,314,702	....	....
Russia, European	7,373,756	....	....
Peanut	191,552,661	46,711,168	....
France	183,175,174	41,295,053	....
Soy bean	17,499,579	....	....
Denmark	7,291,809	....	....
Germany	5,674,385	....	....
United Kingdom	4,533,385	....	....
Sunflower seed	81,659,242	2,848,367	662,041
Denmark	5,395,066	....	....
Germany	5,962,998	....	....
Russia, European	69,709,337	1,529,772	662,041
Turnip and rapeseed	27,985,739	5,189,736	5,044,081
Argentina	314,226	5,189,736	4,272,471
France	3,839,725	....	....
Germany	20,068,835	....	....
Netherlands	1,485,938	....	....
United Kingdom	992,070	....	....
United States	....	....	771,610
Other	927,786	....	....
Denmark	503,718	....	....
Germany	288,926	....	....
Ozokerite	91,685	84,247	26,515
Paraffin:			
Crude	1,884,219	1,505,138	237,310
Denmark	232,171	....	....
United Kingdom	1,252,579	397,075	1,107
United States	288,752	1,108,043	236,203
Refined	4,853,938	3,485,131	1,433,034
Austria	548,945	....	....
Germany	1,569,695	186,540	....
United Kingdom	632,908	466,648	....
United States	1,996,744	2,814,811	1,414,884
Resinous oils	527,589	153,758	....
Belgium	121,220	....	....
Germany	199,653	....	....
United Kingdom	198,965	113,903	....
Stearin (stearic acid)	374,379	232,912	71,861
Belgium	89,754	....	....
Netherlands	255,019	40,829	....
United Kingdom	....	153,561	....
United States	....	36,499	71,105
Tallow:			
"Premier jus"	3,589,007	4,226,653	....
Argentina	19,299	950,818	....
France	904,946	....	....
Germany	593,838	....	....
Netherlands	862,492	....	....
Norway	45,002	1,233,619	....
United Kingdom	318,902	16,426	....
United States	649,861	2,025,789	....
Compressed	943,487	1,000,179	....
Argentina	....	224,636	....
China	112,803	....	....
France	557,303	132,276	....
United Kingdom	124,066	402,185	....
United States	91,564	228,776	....
Other	3,826,246	3,388,391	88,479
Denmark	641,805	....	22,165
France	364,180	165,998	....
Germany	231,005	....	....
Norway	403,310	74,064	....
United Kingdom	1,485,739	528,489	....
United States	388,263	2,597,795	66,279
Textile-dressing preparations containing soap	157,109	97,097	283,247
Turpentine oil	1,136,800	715,280	28,479[1]
Belgium	224,170	....	....
Finland	....	110,239	....
France	590,222	109,320	....
Germany	281,106	....	....
United Kingdom	....	334,491	....
United States	....	155,283	....
Vaseline	778,133	183,672	174,688
Vegetable oils:			
Fixed:			
Coconut and palm kernel:			
Purified	18,731,058	6,718,856	636,457
Belgium	1,332,723	....	....
Denmark	862,060	381	....
Germany	11,602,841	....	....
Netherlands	208,952	2,507,426	....
Norway	463,691	2,315,379	....
Spain	....	....	259,642
United Kingdom	379,244	380,834	270,994
United States	....	62,238	....
Other	9,066,653	2,196,838	46,749
France	4,715,463	917,559	....
Germany	2,411,530	....	....
United Kingdom	1,025,382	738,640	46,749
Cottonseed	5,267,964	11,553,764	....
Germany	324,061	....	....
Netherlands	1,983,205	....	....
Norway	....	1,568,178	....
United Kingdom	799,392	73,841	....
United States	1,955,582	9,911,745	....
Hemp and castor	1,910,621	498,751	20,434
Denmark	708,472	....	....
Germany	277,766	....	....
Netherlands	....	235,700	....
United Kingdom	634,162	238,842	....

[1] Not given by countries.

Imports of Chemicals and Allied Products (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
Oils, Fats, and Waxes (*Concluded*):			
Vegetable oils (*Concluded*):			
Linseed:			
Raw	762,196	560,222	79,048[1]
Belgium	55,294	....	....
Germany	76,967	....	....
Netherlands	625,432	....	....
United Kingdom	....	363,400	....
United States	....	194,089	....
Boiled	30,492	14,367	549,289
Finland	....	....	526,368
Maize	4,950,689	986,475	33,356
United Kingdom	4,026,038	181,333	33,356
United States	427,942	805,142	....
Olive	731,182	1,206,712	88,781
Palm	1,922,030	1,327,189	109,392
Germany	247,603	....	....
United Kingdom	1,642,808	1,326,484	109,392
Peanut	3,123,601	1,390,551	....
France	578,633	1,314,166	....
Germany	1,877,675	....	....
Sesame	4,445,876	310,119	10,079[1]
Germany	3,459,765	....	....
Netherlands	469,946	297,121	....
Soy bean	9,326,366	14,993,004	86,127
China	1,028,660	1,927,142	....
Denmark	2,881,397	1,260,612	....
Germany	1,237,239	....	....
Japan	2,053,907	11,655,868	....
United Kingdom	1,348,849	18,739	86,127
United States	....	130,642	....
Turnip and rapeseed	206,988	411,213	66,451
United Kingdom	167,724	237,411	55,931
United States	....	173,568	....
Other	1,364,522	794,478	40,386
China	392,703	105,380	....
Germany	376,537	....	....
United Kingdom	336,069	353,221	....
United States	57,827	93,133	....
Volatile	54,335	89,368	70,353
France	3,732	10,613	5,168
Germany	41,654	45,847	39,793
Italy	4,107	8,459	4,610
United Kingdom	1,484	13,750	6,334
United States	....	1,021	7,930
Wax:			
Beeswax	35,137	29,531	4,012
Sealing wax	22,901	12,385	1,664
Vegetable (carnauba, palm, etc.)	58,190	221,368	64
France	....	33,283	....
Germany	55,115	....	....
United Kingdom	....	81,579	....
United States	....	47,271	....
Wax manufactures	1,651	1,512	1,085
Wood oil	1,601	1,607	....
Tars, Gums, Resins, Etc.:			
Camphor	44,361	34,694	8,913
Caoutchouc, gutta-percha, etc.:			
Dissolved or paste	296,971	38,728	229
Soft rubber, artificial	43,327	55,230	22,458
Unmanufactured	2,069,628	2,586,159	1,033,536
Denmark	398,305	590,220	1,026,400
Germany	234,931	132	....
United Kingdom	907,021	1,774,807	....
Waste rubber	281,832	291,380	34,334
Coal tar prepared for covering roofs	185,513	48,309	2,418
Dextrin	409,718	50,075	27,057
Gelatin:			
Manufactures	1,570	2,747	417
Sheets	9,251	23,455	15,807
Glue:			
Elastic glue for printing cylinders	44,273	27,571	14,526
Liquid glue and gum	25,194	29,196	41,219
Marine glue, etc., not liquid:			
Agar-agar	17,183	42,075	3,785
Gelatin glue	47,588	57,112	17,077
Isinglass	218	13,774	575
Other	231,779	303,665	277,987
Germany	37,155	91,062	....
Netherlands	....	....	169,610
United Kingdom	110,540	144,266	51,571
Vegetable	1,856	3,821	....
Gum, natural	564,941	708,184	45,142
France	23,916	616,900	32,666
Germany	432,450	....	....
United Kingdom	64,673	73,310	....
Pitch of coal or wood tar	8,720,615	7,331,933	307,447[1]
Germany	389,401	3,014,727	....
United Kingdom	7,887,305	3,865,100	....
Resin soap and tanners' glue	198,291	57,198	....
Belgium	54,537	....	....
United States	124,626	49,017	....
Resins:			
Colophony	6,356,911	5,214,438	113,406
France	302,750	1,286,311	....
Germany	5,137,382	33,237	....
Norway	120,505	957,276	111,854
United States	549,956	2,863,050	....
Copal	303,722	1,080,962	....
Germany	147,884	289	....
Norway	....	521,371	....
United States	....	424,070	....

[1] Not given by countries.

Imports of Chemicals and Allied Products (*Concluded*)

	1913 Pounds	1916 Pounds	1917 Pounds
Tars, Gums, Resins, Etc. (*Concluded*):			
Resins (*Concluded*):			
Shellac	369,076	355,471	87,504
Finland	....	....	49,132
France	....	109,706	....
Germany	219,777	....	....
United Kingdom	139,903	226,734	31,707
Other	8,574,570	13,162,984	13,111[1]
France	318,674	964,946	....
Germany	7,964,465	49,833	....
Norway	....	1,778,892	....
United Kingdom	....	2,727,338	....
United States	....	7,336,478	....
Tar oils	1,367,344	68,142	47,924
Germany	1,270,784	....	....
Terpineol, safrol, and menthol	23,345	60,091	33,027
Germany	20,695	5,256	4,947
United Kingdom	....	52,589	23,029
United States	....	....	3,697
Turpentine	51,074	15,628	2,560
Wood tar and tar water	740,530	2,825,508	1,420[1]
Finland	291,142	2,795,323	....
Russia, European	320,520	....	....
Miscellaneous Materials and Manufactures:			
Asphalt	15,011,196	13,957,137	9,452,148
Germany	13,185,139	9,281,708	7,820,340
United Kingdom	660,957	3,320,335	899,803
United States	....	590,445	372,600
Candles	51,006	152,305	25,562
Explosives	567,744	342,756	180,279
Gases	76,278	51,564	4,506
Carbonic acid	4,742	112	....
Oxygen and hydrogen	5,258	(2)	439
Other	66,278	51,452	4,067
Glass	8,378,995	13,254,494	11,323,304
Gypsum, precipitated	152,897	93,714	916,693
Germany	....	....	916,693
Insulating material	368,702	671,693	578,802
Germany	329,799	621,805	575,685
Mica, unmanufactured	78,903	237,733	81,511
	Metric Tons	Metric Tons	Metric Tons
Ores, etc.:			
Copper	10	773	555
Graphite	576	719	668
Germany	413	483	629
United Kingdom	....	111	28
Iron	2,909	34	....
Magnesite and witherite	962	992	948
Manganese	854	276	....
Germany	791	5	....
United States	....	246	....
Sulfur pyrites	141,005	128,005	103,894
Norway	86,416	124,312	102,443
Spain	25,102	3,661	1,451
Zinc	12,628	12	....
Other	181	6,309	2,136
	Pounds	Pounds	Pounds
Paper and pulp:			
Cardboard	8,374,480	2,884,712	1,320,311
Paper	5,461,526	8,387,967	4,863,647
News print	....	43,697	....
	Metric Tons	Metric Tons	Metric Tons
Pulp	4,947	4,128	1,552
	Pounds	Pounds	Pounds
Polishes for leather goods	257,585	84,101	25,390
Putty	127,554	74,961	23,823
Soap:			
Perfumed	35,126	104,405	111,890
Soft	56,277	26,235	7,035
Other	735,501	1,972,890	572,246
Finland	....	....	213,033
France	104,829	380,503	....
Germany	80,926	28,651	....
United Kingdom	520,292	1,285,447	312,046
United States	....	256,618	....
Sugar	4,751,410	582,812	15,666,948
Vinegar and acetic acid	136,621	98,819	80,558
Washing, cleansing, and polishing substances	480,548	263,046	202,810
Germany	248,108	41,219	....
United Kingdom	171,840	195,065	147,583

[1] Not given by countries.
[2] Not stated separately.

STATISTICS OF EXPORTS

The export returns have been compiled from the same sources as the import figures—that is, a summary table has been based upon late monthly statistics and covers the years 1913, 1918, and 1919, while the detailed table has been compiled from the annual publications for 1913, 1916, and 1917. These publications are issued by the Swedish Department of Commerce, of the Board of Trade.

SUMMARY OF EXPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1918 Pounds	1919 Pounds
Chalk, ground, washed, or precipitated	19,683,467	11,640,689	7,618,037
Chemicals, drugs, etc.:			
Calcium and barium carbide	....	8,934,408	6,330,635
Copper sulfate	551,796	662,156	464,434
Fertilizers:			
Cyanamide	....	848,991	1,230
Superphosphate	79,447,146	....	24,600,029
Potassium and sodium chlorate	3,281,675[1]	1,428,717	114,710
Methanol, raw and refined	856,461	14,716	585,057
Glass flasks and bottles	28,526,157	8,473,526	12,643,571
Matches:			
Safety	61,208,799	62,845,247	60,509,517
Other	15,491,521	27,948	2,149,763
Oils, fats, and waxes:			
Rubber waste	1,400,148	894,433	61,925
Tallow	1,160,261	....	17,674
Turpentine oil	488,522	69,169	734,324
Ores:	Metric Tons	Metric Tons	Metric Tons
Iron	6,439,950	4,485,500	2,418,989
Zinc	47,191	16,210	55,138
Paper and pulp:			
Pulp	1,006,456	714,306	902,497
	Pounds	Pounds	Pounds
Cardboard	56,690,440	45,081,574	45,112,423
Paper	409,736,822	283,996,245	307,431,434
News print	135,694,285	94,190,834	145,650,850
Tars, gums, and resins:			
Wood tar and tar water	17,066,399	9,948,518	18,138,466

[1] Potassium chlorate only.

Following is the detailed table of exports compiled from the latest official annual publications. Of special interest are the figures showing the extent to which Germany depended upon Sweden for certain essentials during the war.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC.:			
Acetate of lime	1,775,274	605,284	95,453
Denmark	591,135	119,117	....
Germany	....	66,929	....
Norway	....	....	95,453
United Kingdom	995,659	419,238	....
Acids:			
Boric	485	18,289	1,726
Citric and tartaric	2,665	138,493	....
Russia, European	....	121,930	....
Hydrochloric	1,819	860,696	2,618,168
Denmark	....	522,839	1,976,278
Norway	....	359,903	444,778
Hydrofluoric acid and fluoride of ammonium	....	20,152	1,250
Nitric	....	200,738	63,263[1]
Austria	....	57,655	....
Finland	....	80,298	....
Oxalic	635	847,111	410,635
Finland	....	219,133	....
France	....	103,621	201,465
Russia, European	....	410,611	....
United States	....	33,067	98,685
Phosphoric	145,098	218,061	122,086
Denmark	....	68,303	....
Norway	107,357	91,489	89,401
Russia, European	....	44,443	....
Sulfuric:			
Fuming	1,452,459	259,660	398,411
Norway	1,452,459	251,075	397,088
Other	140,323[1]	3,087,392	3,530,704
Denmark	....	637,050	2,050,327
Norway	....	2,384,354	1,470,111
Albumin	....	18,078	....
Germany	....	15,873	....
Alum	13,534[1]	265,354	298,053
Denmark	....	190,546	200,127
Aluminium sulfate	1,398,080	18,377,078	19,978,758
Denmark	1,351,640	2,722,240	1,390,867
Finland	....	7,946,176	14,604,959
Norway	....	6,095,410	2,968,527
Russia	....	1,613,251	1,014,405
Ammonia:			
Caustic	14,286[1]	82,838	194,735
Norway	....	51,691	123,676
Sal ammoniac	2,013	138,755	33,208
Sulfate	560,848	1,609	....
Germany	560,630	....	....
Ammonium, potassium and sodium phosphate	1,433	88,638	....
Germany	....	88,638	....
Arsenic, white	....	7,308	....
Barium protoxide (baryta) and barium peroxide (gray powder)	....	123,647	....
Russia, European	....	123,647	....
Borax	8,563[1]	175,742	....
Austria	....	47,070	....
Germany	....	118,870	....
CHEMICALS, DRUGS, ETC. (*Continued*):			
Calcium and barium carbide	29,954,634	32,430,250	28,505,776
Belgium	2,430,020	....	286,601
British South Africa	487,217	....	....
Chile	....	467,380	....
Denmark	709,286	1,899,814	1,358,047
Finland	....	718,810	....
Germany	4,495,270	5,509,736	14,262,902
Netherlands	1,660,081	10,439,828	7,175,973
Norway	4,244,098	....	....
Portugal	1,321,437	....	....
Russia, European	....	6,349,998	1,440,486
United Kingdom	14,131,473	6,837,457	3,548,138
Calcium, barium and aluminium chloride	....	777,366	264,290[1]
Finland	....	274,151	....
Russia, European	....	450,442	....
Carbon disulfide and chloride of sulfur	....	44,313	....
Russia, European	....	44,092	....
Carborundum	....	291,252	35,770
Finland	....	202,572	....
Germany	....	71,731	....
Russia, European	....	....	23,589
Casein	329,835	332,542	114,390
Denmark	139,203	....	....
Germany	143,784	295,262	114,390
Chemical products not specifically mentioned	802,847	3,012,335	4,344,469
Germany	127,677	260,136	1,077,853
United Kingdom	505,378	2,384,579	3,160,989
United States	....	107,099	....
Chloride of lime	180,987	....	85,980
Copper:			
Oxide	159,889	469,988	626,990
Germany	159,889	398,684	602,508
Sulfate	551,796	1,543,308	1,388,237
Austria	....	418,654	1,167,997
Germany	356,358	....	....
Hungary	....	1,124,655	....
Russia, European	184,194	....	....
Turkey, European	....	....	220,242
Drugs and toilet preparations:			
Drugs	14,842	21,702	30,075
Finland	....	2,233	7,681
Germany	6,715	....	....
Russia, European	....	12,286	17,344
Hair dye	3,349	10,946	3,975
Perfumery and cosmetics	9,185	23,532	11,115
Toilet water	28,073	39,271	36,947
Tooth powder and paste	14,352	15,604	7,019
Fertilizers:			
Cyanamide	37,323,444	42,600,004	6,428,455
Germany	33,399,029	42,554,589	6,428,455
Potash salts	42,770	....	....
Sodium nitrate	2,315	....	5,500
Superphosphate	79,447,166	365,967	670,397
Denmark	39,280,306	365,967	670,397
Finland	5,724,614	....	....
Russia, European	34,429,448	....	....
Thomas phosphate and slag	4,070,904	....	....
Finland	1,269,863	....	....
Russia, European	2,777,824	....	....
Formalin solution	145,704	277,733	467,977
Denmark	84,665	6,537	65,016
Finland	....	90,345	32,297
Germany	....	89,904	275,875
Japan	46,297	....	....
Netherlands	....	22,602	57,470
Glycerol:			
Crude	398,369	5,291	88,185
Germany	393,559	....	88,185
Refined	7,476[1]	269,669	96,903
Denmark	....	44,169	39,683
Norway	....	114,059	37,465
United Kingdom	....	111,440	....
Hydrogen peroxide	397	142,902	61,619
Russia, European	....	138,273	60,075
Iron oxyhydrate	2,579,733	44,092	1,130,475
Iron sulfate	16,867	28,563	992
Lead oxide and peroxide	117,375	885,301	9,724[1]
Germany	99,022	321,466	....
Russia, European	....	556,937	....
Magnesia, calcined or carbonate	....	146,789	130,567
Russia, European	....	123,200	94,158
Magnesium:			
Chloride	84	4,031,918	420,732
Finland	....	955,419	....
Norway	....	....	22,046
Russia, European	....	3,050,869	398,686
Sulfate	1,102	171,538	168,542
Methanol:			
Crude	798,645	564,975	286,064
Germany	675,132	510,039	260,886
Refined	86,328	76,702	91,736
Nitrobenzene	....	78,501	48,051
Denmark	....	20,692	24,777
Norway	....	57,809	23,274
Phosphorus	1,984	6,453	....
Potash	....	306,849	18,254
Norway	....	89,822	....
United Kingdom	....	157,682	....
United States	....	55,080	....

[1] Not given by countries.

[1] Not given by countries.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
CHEMICALS, DRUGS, ETC. (*Concluded*):			
Potash, yellow prussiate of	224,924	196,952	57,465
Russia, European	....	155,702	53,563
United States	112,531	....	....
Potassium chromate	5,172	8,461	....
Potassium and sodium:			
Hydroxide	540,943	900,024	210,004
Solid	539,305	733,971	143,665
Finland	....	106,154	....
Germany	145,801	....	....
Norway	....	171,868	....
Russia	....	89,154	....
United Kingdom	102,252	112,468	....
United States	....	163,350	56,912
Liquid	1,638	166,053	66,339
Chlorate	3,137,384[1]	1,492,400	2,494,492
Denmark	....	417,803	336,396
Germany	708,499	193,125	1,673,308
Japan	745,743	....	....
Norway	560,026	257,585	....
Russia, European	193,187	377,306	125,884
United Kingdom	760,972	141,112	6,614
Cyanide	4	4,566	7,987
Sulfide	1,369	438,482	103,314
Finland	....	130,916	....
Russia, European	....	282,416	....
Rennet	142,790	98,964	73,810
Australia	89,419	58,312	53,290
Salt, table	15,247	3,724,193	....
Finland	....	3,692,429	....
Soda	3,333	116,760	....
Norway	....	47,375	....
Sodium:			
Chlorate	871,686	....	....
Germany	209,439	....	....
Russia, European	496,040	....	....
Sulfate and bisulfate	1,143,548	17,116,918	101,749[2]
Finland	....	17,022,248	....
Germany	796,081	....	....
Sulfite	117	294,257	304,241
Denmark	....	....	25,128
Finland	....	73,036	....
Norway	....	....	219,192
Russia, European	....	183,407	....
Stannous chloride, stannic chloride, and putty powder	19,676	60,463	....
Sugar of lead and lead vinegar	29,537	10,064	....
Sulfur	525,947	....	2,205[2]
Norway	503,780	....	....
Tartar	2,608	168,019	51,297
Germany	....	166,295	150,706
Water glass	....	232,127	193,251[2]
Russia, European	....	118,449	....
Zinc sulfate and zinc chloride	....	13,371	15,814
COLORS AND DYES:			
Butter and cheese coloring	119,203	215,101	66,464
Colors for printing	29,469	133,700	31,215
Denmark	6,945	48,400	6,025
Finland	11,358	55,834	6,100
Norway	11,135	....	19,090
Colors prepared with oil	36,230	151,599	3,040
Dyestuffs, vegetable	3,172	29,323	3,307
Earth colors	13,574	1,598,563	922,449
Inks:			
Printer's, black	67,214	477,089	2,498
Other	179,995	149,520	99,183
Denmark	43,115	48,400	....
Finland	53,173	55,834	49,204
Germany	31,001	....	....
Norway	50,152	....	....
Russia	....	22,740	11,041
Lampblack	697,985	1,057,092	599,378
Denmark	251,574	393,658	355,159
Norway	183,974	146,275	....
Mineral colors:			
Red lead	12,615[2]	1,183,654	92,595
Finland	....	722,595	70,203
Russia, European	....	439,013	22,392
Red ocher	795,894	1,114,743	644,748
Finland	737,053	1,082,847	643,900
White lead	28,642[2]	717,419	43,982
Finland	....	298,309	....
Russia, European	....	419,110	43,541
Zinc sulfide and white baryta	11,038[2]	3,884,805	380,734
Finland	....	611,336	....
Russia, European	....	3,273,469	303,133
Zinc white	99,661	7,956,124	4,351,938
Denmark	53,627	....	22,046
Finland	....	2,234,170	1,434,877
Germany	....	167,276	....
Norway	....	26,676	752,540
Russia, European	....	5,528,001	2,142,474
Other	18,538[2]	844,170	322,350
Finland	....	337,127	211,902
Russia, European	....	44,070	107,834
Tar colors	7,315[2]	16,252	170,389
Finland	....	5,611	116,615
Russia, European	....	10,318	53,708
Varnish:			
Oil	19,217	105,195	....
Spirit	8,241	29,513	2,383
Other	82,975	309,438	89,489
Finland	32,205	37,844	....
Norway	27,053	199,056	88,918
Other colors, dyes, etc.	19,006	364,493	139,743

[1] All potassium chlorate.

[2] Not given by countries.

EXPORTS OF CHEMICALS AND ALLIED PRODUCTS (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
OILS, FATS, AND WAXES:			
Acetone and acetone oil	24,233[1]	153,773	79,952
Denmark	....	8,940	20,977
Finland	....	28,825	....
Germany	....	....	34,193
Norway	....	44,749	20,587
Russia, European	....	39,939	....
Animal fat:			
Bone fat	343,640	1,055,774	....
Germany	320,871	1,055,774	....
Other	134,214	....	472,424
Germany	54,846	....	472,424
United Kingdom	76,341	....	....
Animal oils:			
Fish oils	245,837	428,177	147,146
Germany	238,639	273,121	147,146
Other	92,516[1]	319,954	466,579
Germany	....	289,354	442,827
Degras (tanner's fat)	51,865	....	....
Lubricating substances not elsewhere specified	52,943	345,293	....
Germany	....	315,745	....
Machine and wagon grease	23,084	4,032	....
Mineral oils:			
Crude	93,287	....	40,786
Refined:			
Benzine and gasoline	4,324,376	....	....
Denmark	2,521,734	....	....
Norway	1,802,642	....	....
Illuminating oils	6,758,124	3,375[1]	9,921[1]
Denmark	6,076,237	....	....
Norway	672,705	....	....
Lubricating oils:			
Light	1,122,419	32,752	....
Denmark	824,185	....	....
Norway	220,716	....	....
Dark	64,749	2,627,056	1,388,900
Germany	....	2,627,056	1,388,900
Other	22,304	1,508	....
Oilcake	4,565,740	....	....
Olein	576,465	62,507	188,496
Denmark	68,210	....	....
Finland	76,447	....	....
Germany	336,336	62,507	188,496
Paraffin	3,600	8,534	....
Resinous oils	74,319	....	....
Stearin (stearic acid)	60,278	7,727	....
Tallow	1,180,233	67,009	263,494
Denmark	318,139	....	....
Germany	579,755	66,899	263,494
Norway	264,283	....	....
Textile-dressing preparations containing soap	9,169	6,717	441
Turpentine oil	503,224	1,034,405	840,305
Denmark	....	....	190,533
Germany	301,056	898,088	649,744
United Kingdom	152,995	....	....
Vaseline	866	69,731	....
Germany	....	60,981	....
Vegetable oils:			
Fixed:			
Cottonseed	21,385	279,351	30,953
Germany	....	266,234	30,953
Hemp and castor	608	196,831	....
Germany	....	191,115	....
Linseed:			
Raw	1,585	1,828,616	....
Germany	....	1,828,616	....
Boiled	1,969	95,300	....
Germany	....	94,672	....
Maize	....	679,678	....
Germany	....	679,678	....
Olive	622	705,763	....
Germany	....	354,059	....
Russia, European	....	255,817	....
Soy bean	....	352,932	....
Germany	....	352,932	....
Turnip and rapeseed	1,179	1,832	....
Other	582,268	487,752	79,273
Denmark	374,985	....	....
Germany	158,733	402,818	79,273
Volatile	2,112	18,821	13,975
TARS, GUMS, AND RESINS:			
Benzene oils:			
Carbolic acid, cresol, and creosote oil	6,669	11,230	....
Carbolineum	37,425	60,219	....
Naphthalene	456	497,534	45,673
Finland	....	166,747	....
Russia, European	....	330,787	....
Other	8,800	6,426	871
Caoutchouc and gutta-percha:			
Crude	439	32,483	9,691
Germany	....	32,483	9,691
Dissolved or paste	83,034	33	110
Norway	42,659	....	....
Russia, European	34,826	....	....
Coal tar	3,434,377	1,654,178	4,327,941
Finland	1,851,883	1,597,868	....
Germany	....	....	4,199,794
Norway	....	....	128,147
Russia, European	1,362,749	....	....
Coal tar prepared for covering roofs	639,945	796,784	....
Finland	560,273	425,179	....
Norway	....	187,717	....

[1] Not given by countries.

Exports of Chemicals and Allied Products (*Continued*)

	1913 Pounds	1916 Pounds	1917 Pounds
Tars, Gums, and Resins (*Concluded*):			
Dextrin:			
Solid	3,166	17,635	88
Liquid	55,016	800,268	28,248
Denmark	....	150,305	....
Norway	....	559,170	....
Gelatin, in sheets	....	7,725	....
Glue:			
For printing cylinders	14,088	15,273	1,843
Liquid	1,847	78,642	4,806
Not liquid:			
Agar-agar	....	19,652	....
Germany	....	14,032	....
Gelatin glue	214	5,042	....
Isinglass	....	4,504	6,237
Other	72,811	212,612	....
Vegetable	2,458	1,276	....
Gum, natural	3,056	183,409	22,046
Austria	....	46,519	....
Germany	....	108,195	22,046
Pitch of coal or wood tar	305,644	3,091,043	174,911
Finland	....	1,320,101	....
Germany	....	1,470,803	114,584
United Kingdom	188,222	....	....
Resins:			
Colophony	7,083	80,503	....
Germany	....	59,537	....
Copal	66	10,518	....
Shellac	1,060	7,271	....
Other	10,957[1]	6,817,580	3,065,351
Austria	....	418,537	32,143
Finland	....	203,412	55,151
Germany	....	5,862,221	2,973,450
Hungary	....	125,038	....
Russia, European	....	134,692	....
Resin soap and tanners' glue	1,769,176	1,577,918	662,604
Denmark	844,796	....	....
Germany	194,613	1,484,185	662,604
Netherlands	113,713	....	....
United Kingdom	560,564	....	....
Rubber waste	1,396,949	1,707,046	2,715,051
Denmark	516,216	600,981	1,360,721
Germany	167,259	1,042,666	1,354,330
United States	582,180	....	....
Tar oils	1,209,159	1,406,089	508,548
Austria	....	198,533	....
Germany	202,325	933,029	364,101
Hungary	....	97,948	....
United Kingdom	891,970	37,699	8,819
Terpineol, safrol, and menthol	280	24,182	6,579
Austria	....	4,993	....
Germany	....	16,486	4,870
Hungary	....	2,381	....
Turpentine	44,357	13,676,029	5,966,499
Germany	3,448	13,573,288	5,884,684
United Kingdom	40,909	....	....
Wax (beeswax, carnauba, etc.)	5,035	13,642	82
Wood tar and tar water	17,627,605	23,630,951	15,289,016
Belgium	1,551,035	73,855	....
Denmark	1,035,935	1,798,678	1,060,078
France	4,523,220	1,212,127	....
Germany	2,416,696	9,243,978	11,293,758
Netherlands	1,903,020	3,084,579	320,589
Norway	2,441,400	5,816,257	2,404,950
United Kingdom	2,319,539	390,618	....
Ores, Etc.:	Metric Tons	Metric Tons	Metric Tons
Antimony	7	....	....
Copper	1,709	2,278	....
Graphite	48	9	3
Iron	6,439,750	5,536,641	5,818,498
Belgium	231,647	....	....
Germany	4,977,395	4,298,586	4,824,748
Norway	11,391	168,393	954,694
United Kingdom	672,836	846,222	....
United States	361,215	217,236	....
Magnesite and witherite	1,249	4,989	6,291
Mica	....	25	8
Sulfur pyrites	500	14,003	29,800
Germany	100	13,992	29,799
Zinc	46,696	9,351	6,804
Belgium	23,211	....	....
France	10,585	....	....
Germany	11,845	9,351	2,167
Netherlands	....	....	4,387
Other	4,478	1,376	549

[1] Not given by countries.

Exports of Chemicals and Allied Products (*Concluded*)

Articles	1913 Pounds	1916 Pounds	1917 Pounds
Miscellaneous Materials and Manufactures:			
Candles	78,691	9,251	....
Chalk, ground, washed or precipitated	20,921,956	13,683,679	16,687,768
Brazil	....	1,416,400	....
Finland	1,632,206	2,966,016	975,319
Germany	15,658,149	4,280,980	10,802,159
Netherlands	....	1,817,913	....
Norway	1,830,127	1,761,892	2,547,691
Explosives	316,720	1,103,579	798,600
Gases:			
Coal gas	88,609	4,916	13,625
Oxygen and hydrogen gas	118,374	650,394	2,090,243
Denmark	109,476	623,498	1,990,009
Other	623,908	833,385	454,531
Australia	39,110	114,562	65,884
Denmark	21,202	53,047	76,899
Hungary	64,617	....	....
Norway	12,035	37,240	85,027
Russia, European	22,266	223,187	20,227
United States	298,845	212,329	110,672
Glass	28,482,475	33,786,561	14,546,329
Flasks and bottles	28,464,776	31,947,928	12,809,755
Insulating material	96,032	51,048	81,919
Matches:			
Safety	61,251,599	108,967,423	85,101,694
Austria	49,604	2,779,022	150,729
British India	5,479,103	....	....
Denmark	512,371	1,129,489	2,780,307
Finland	....	1,640,632	3,727,128
Germany	7,582,208	15,525,351	6,741,327
Netherlands	1,850,343	6,073,871	7,848,713
Russia, European	....	12,010,493	25,927,946
United Kingdom	24,444,208	56,536,041	30,966,226
United States	7,286,188	2,839,439	4,722,542
Other	15,060,463	9,051,082	2,077,908
British India	6,826,511	....	....
United Kingdom	6,663,434	7,722,566	20,236,631
Paper and pulp:			
Cardboard	57,137,884	94,312,364	42,273,557
Paper	418,023,082	489,731,781	260,526,131
	Metric Tons	Metric Tons	Metric Tons
Pulp	1,009,359	1,009,163	695,948
Polishes for leather goods:	Pounds	Pounds	Pounds
Blacking	1,883	197,975	14,603
Finland	....	175,879	14,383
Wax	9,687	23,673	....
Other	156,683	235,345	3,768
Finland	....	59,709	....
Norway	....	44,912	....
Russia	101,196	106,897	....
Putty	46,731	786,724	49,919
Finland	31,034	....	....
Germany	....	759,906	22,046
Soap:			
Perfumed	31,660	80,964	4,087
Finland	22,381	39,330	....
Germany	....	34,158	....
Soft	38,329	1,401,178	690
Germany	....	1,401,178	....
Other	10,366	629,568	880
Austria	....	264,555	....
Germany	....	347,518	....
Vinegar and acetic acid in casks:			
Up to 10% acid content	1,642	72,011	38,424
Of higher acid content	210,288	43,078	259,541
Denmark	....	....	72,675
Netherlands	....	....	109,716
United Kingdom	173,586	....	....
In other containers	132,049[1]	424,826	313,258
Austria	....	103,094	105,179
Germany	....	100,029	30,459
Hungary	....	94,264	65,763
Netherlands	....	....	....
United Kingdom	....	69,235	109,652
Washing, cleansing, and polishing preparations	802,662	616,503	58,594

[1] Not given by countries.

CONTRIBUTIONS FROM THE CHEMICAL WARFARE SERVICE, U. S. A.

A METHOD FOR DETERMINING THE SULFUR MONOCHLORIDE CONTENT OF MUSTARD GAS-S_2Cl_2 MIXTURES[1]

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In the manufacture of mustard gas (β,β-dichloroethyl sulfide) from sulfur monochloride and ethylene by the improved Levinstein process as employed at Edgewood Arsenal, the sulfur monochloride content of the reaction mixture is kept constant or is varied as is required by the rate of absorption of ethylene, the temperature, or the capacity of the cooling system. This S_2Cl_2 concentration is generally kept between 25 and 30 per cent throughout the run until

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all the S_2Cl_2 has been added; it is then gradually decreased until practically zero. During the entire operation it is essential that an accurate knowledge of the S_2Cl_2 content be available in order to secure the conditions for a maximum rate of absorption of ethylene and to avoid the reaction "running wild" and spoiling the entire charge. Observations of the S_2Cl_2 content were required every 20 min.; hence a quick method of determining its concentrations in the mustard gas had to be devised. If it had been possible to measure accurately the amount of ethylene absorbed, it would have been possible to calculate the S_2Cl_2 content from a knowledge of the initial charge of mustard gas and the S_2Cl_2 added. Curves which gave this information for any particular initial charge of mustard gas were constructed, but the measurement of large volumes of effluent gases of corrosive nature was not feasible; hence a quick chemical control became necessary.

The method devised and used at the Edgewood Plant of Edgewood Arsenal is based upon the liberation of iodine from sodium iodide by means of sulfur monochloride. The data seem to establish quite firmly the fact that the liberation of iodine is in accordance with the equation

$$S_2Cl_2 + 2\,NaI = I_2 + 2\,S + 2\,NaCl \qquad (1)$$

The iodine liberated was titrated with a standard sodium thiosulfate solution, and from the data obtained the sulfur monochloride weight was calculated according to the above equation.

The only reference so far found in the literature regarding the reaction between iodides and sulfur monochloride was the work of Hautefeuille,[1] who stated that the reaction between anhydrous hydriodic acid and sulfur monochloride was quite vigorous at room temperature, yielding hydrochloric acid, free iodine, the iodide of sulfur, and finally, with an excess of hydriodic acid, hydrogen sulfide. Hautefeuille does not give any definite equations for the reactions described; but if the formation of the iodide of sulfur be regarded merely as metathetical, the equation which would probably describe his results would be

$$S_2Cl_2 + 6\,HI = 2\,HCl + 2\,H_2S + 3\,I_2. \qquad (2)$$

But if it be considered that in a water solution, as in the proposed method, hydrogen sulfide reacts with iodine to form hydriodic acid and free sulfur according to the equation

$$2\,H_2S + 2\,I^\circ_2 = 4\,HI + 2\,S^\circ \qquad (3)$$

the addition of Equation 3 to Equation 2 represents the reaction which would take place when a water solution of hydriodic acid is placed in contact with sulfur monochloride.

$$S_2Cl_2 + 2\,HI = 2\,I^\circ + 2\,S + 2\,HCl \qquad (4)$$

By inspection, it is seen that Equations 1 and 4 both call for the liberation of one molecule of free iodine for every molecule of sulfur monochloride used.

ACCURACY ATTAINABLE AND REQUIRED—The sulfur monochloride used in this investigation was prepared by carefully refluxing crude sulfur monochloride with an excess of sulfur and then distilling off the sulfur chloride from this excess. The distillate was redistilled, the fraction coming over between 137.5° and 138.5° C. being collected for use. The purified sulfur monochloride was weighed (in small tipped glass bulbs, sealed after filling), dissolved in carbon tetrachloride, and diluted to obtain weight per cent solutions ranging from 0.02 to 25 per cent S_2Cl_2.

The accuracy of the determination based upon Equation 1 is shown by the following tabular presentation of the experimental data:

Conc. Per cent	Wt. S_2Cl_2 in Sample	Wt. S_2Cl_2 Determined by Titration	Variation Gram	Error Per cent	Error in Conc. Per cent
0.02	0.03041	0.02884	—0.00157	5.16	0.001
0.04	0.03041	0.02917	—0.00124	4.08	0.002
0.10	0.03041	0.02982	—0.00059	1.80	0.002
0.20	0.03041	0.03045	+0.00004	0.14	0.000
0.40	0.03041	0.03039	—0.00002	0.07	0.000
0.80	0.06082	0.06041	—0.00041	0.67	0.005
1.00	0.03041	0.02984	—0.00057	1.87	0.019
2.00	0.03041	0.02975	—0.00066	2.17	0.043
3.00	0.22869	0.22033	—0.00800	3.50	0.105
7.50	0.22869	0.22139	—0.00730	3.19	0.239
10.00	0.44990	0.43800	—0.01190	2.65	0.265
15.00	0.44990	0.43810	—0.01180	2.62	0.393
25.00	0.44990	0.44350	—0.00640	1.42	0.355

Determinations were also made by using mustard gas as the solvent for the sulfur monochloride, in order to duplicate plant conditions. Since, however, sulfur monochloride itself reacts with mustard gas to yield chlorinated mustard gas (at a rate proportional to the S_2Cl_2 concentration), the determinations at high concentrations (20 to 30 per cent) of sulfur monochloride must be made quickly to yield accurate results. An additional source of error lies in the reaction between the sulfur monochloride and the ethylene dissolved in the reaction mixture, which again calls for a rapid determination of the S_2Cl_2 content at its higher concentrations.

The conditions of the Levinstein process are such as to require a knowledge of the sulfur chloride content with an accuracy of only about one per cent, *i. e.*, it is practically immaterial, as far as operating conditions go, whether the S_2Cl_2 is reported as 24 or 26 per cent, when it is in reality 25 per cent. The determination of the S_2Cl_2 content by this method is accurate to at least one-half per cent at the higher concentrations of sulfur monochloride (20 to 30 per cent), and to about one-tenth per cent at lower concentrations (2 to 5 per cent). An inspection of the last column of the table will serve to illustrate these statements. The method is reliable for sulfur monochloride concentrations as low as 0.04 per cent. The main factor in an accurate determination in the Levinstein plant control operations is the *time* which elapses between the drawing of the sample and its introduction into the sodium iodide solution. In view of such requirements and conditions, the following procedure has been adopted, as it yields results which are certainly made with an accuracy required by the plant operation of the Levinstein process.

METHOD OF PROCEDURE

The method is outlined in order to show under what conditions it was employed. In a glass-stoppered Erlenmeyer flask of 250 cc. capacity are placed about 25 cc. of an approximately normal solution of sodium iodide and 10 cc. of carbon tetrachloride. The flask is then weighed accurately to the second decimal place.

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[1] *Bull. soc. chim.*, [2] 7 (1867), 198.

The sample of the mustard gas-S_2Cl_2 mixture is then quickly introduced into the flask by means of a 2 cc. immersion pipet, and the flask is weighed again; this yields a sample of about 2.5 g. A known excess of a standard sodium thiosulfate solution is added, and the excess is titrated with a standard iodine solution, using starch as an indicator. It has been found that this back titration is quicker and yields more uniform results than does the single direct titration with thiosulfate solution. The number of cc. of thiosulfate solution used, multiplied by its S_2Cl_2 equivalent in grams, yields at once the S_2Cl_2 content of the sample. From these data the percentage composition of the mustard gas-S_2Cl_2 mixture can be calculated.

SUMMARY

1—The need of a chemical control of the sulfur monochloride content in the reaction mixture of the Levinstein process for mustard gas has been pointed out.

2—The availability of iodine liberation by sulfur monochloride as a means for determining the sulfur monochloride is discussed.

3—The accuracy obtainable and the accuracy required by plant operations are presented.

4—The procedure for control operations is outlined.

ACKNOWLEDGMENT

The writers wish to express their appreciation of the help and suggestions of Major Wm. Lloyd Evans, of the chemical laboratory of Edgewood Arsenal.

PRESSURES PRODUCED BY THE ACTION OF SULFUR MONOCHLORIDE UPON β,β'-DICHLOROETHYL SULFIDE[1]

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The purpose of this investigation was to measure the pressures produced when relatively small concentrations of sulfur monochloride reacted with β,β'-dichloroethyl sulfide.

EXPERIMENTAL

The apparatus consisted of manometers connected with pear-shaped flasks containing varying concentrations of sulfur monochloride and β,β'-dichloroethyl sulfide. The latter substance was prepared by double vacuum distillation of the crude commercial product over calcium chloride. After the second distillation it showed a melting point of 13.6° C. The sulfur monochloride was purified by distillation at 136° to 138°.

All proper precautions were taken to see that the apparatus was absolutely dry. In sealing the flasks to the manometers, a long calcium chloride tube was used by the glass blower.

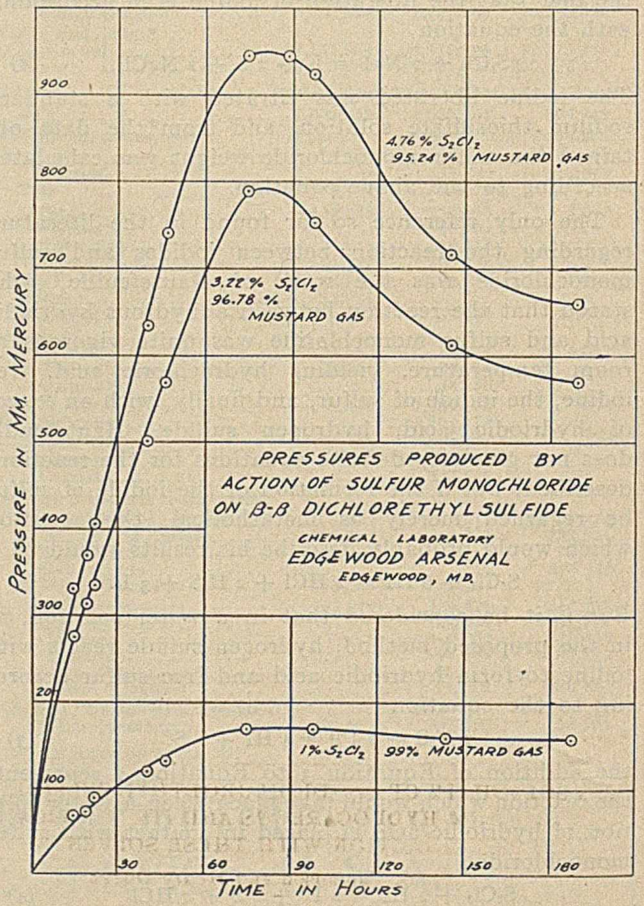
The actual volumes of the flasks, together with the portions of the tubes not filled with mercury and composing an arm of each manometer, were measured. Proper volume corrections were made for the changing of the mercury in the arms of the manometers connected with the flasks.

Four different experiments were run. In each case, the time, temperature, and barometric pressure were recorded every time readings of the manometer were made.

Expt. 1 served as a blank and was run with 50.4 g. of the pure mustard gas in the flask. The data are given in Table I. Expt. 2, the data for which are found in Table II, consisted of a mixture of 64.0 g. of the dichloroethyl sulfide with 0.64 g. of sulfur monochloride. Expt. 3 (Table III) contained 41.1 g. of the pure mustard gas (96.78 per cent) and 1.37 g. of sulfur monochloride (3.22 per cent). Expt. 4 (Table IV) consisted of 49.4 g. of the pure mustard gas (95.24 per cent) and 2.47 g. of sulfur monochloride (4.76 per cent).

TABLE I—PURE β,β'-DICHLOROETHYL SULFIDE

Time Hrs.	Temp. ° C.	Pressure Mm.	Volume N. P. T.	Decreased Volume Cc.
0	18	751	66.4	0.0
16	17	745	66.1	0.3
19	18	748	66.1	0.3
22	20	753	66.1	0.3
40	18	746	66.0	0.4
46	21	756	66.1	0.3
72	25	767	66.2	0.2
89	22	760	66.3	0.1
96	24	763	66.1	0.3
144	21	758	66.3	0.1
189	20	750	66.0	0.4



The tables show that a maximum pressure is reached in approximately 72 hrs., after which time a steady decrease is noted. In several previous experiments the same decrease in pressure had been observed at the end of 72 hrs. when rubber connections were used. Repetition of these experiments with glass-sealed joints showed that this was not due to faulty joints or action of the gases on the rubber.

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TABLE II—1.00 PER CENT SULFUR MONOCHLORIDE : 99.00 PER CENT β,β'-DICHLOROETHYL SULFIDE

Time Hrs.	Temp. ° C.	Barometric Pressure Mm.	Manometer Reading Mm.	Increase Pressure Mm.	Volume N. P. T. Cc.	Increase per Unit Volume Cc.	Increase Pressure V_0T_0 Mm.	Pressure 100 G. Mustard Gas Mm.
0	18	...	762	...	134	0	0	0
16	17	772.5	796.5	24	141	5.2	40	64.5
19	18	772.5	806	34	142	6.0	46	71.8
25	21	771	830	59	145	8.0	61	95.4
40	18	768	833	65	147	9.3	74	115.6
46	19	767	850	83	149	11.2	85	132.8
70	19	765	860	95	153	14.2	108	170
96	24	761	880	119	153	14.2	108	170
136	19	765	857	92	152	13.4	102	160
187	20	767	862	95	152	13.4	102	160

TABLE III—3.22 PER CENT SULFUR MONOCHLORIDE : 96.78 PER CENT β,β'-DICHLOROETHYL SULFIDE

Time Hrs.	Temp. ° C	Barometric Pressure Mm.	Manometer Reading Mm.	Increase Pressure Mm.	Volume N. P. T. Cc.	Increase per Unit Volume Cc.	Increase Pressure V_0T_0 Mm.	Pressure 100 G. Mustard Gas Mm.
0	18	...	760	0	143	0	0	0
16	17	772.5	863	90	164	14.7	112	273
19	18	772.5	884	112	167	16.8	128	312
22	20	771	907	136	169	18.2	138	336
40	18	768	960	192	182	27.2	206	502
46	19	767	995	228	187	30.8	234	570
72	25	764	1089	325	204	42.7	325	791
96	24	761	1074	303	201	40.6	309	753
144	21	760	1010	250	190	32.9	250	609
187	20	767	990	223	187	30.8	234	570

TABLE IV—4.76 PER CENT SULFUR MONOCHLORIDE : 95.24 PER CENT β,β'-DICHLOROETHYL SULFIDE

Time Hrs.	Temp. ° C.	Barometric Pressure Mm.	Manometer Reading Mm.	Increase Pressure Mm.	Volume N. P. T. Cc.	Increase per Unit Volume Cc.	Increase Pressure V_0T_0 Mm.	Pressure 100 G. Mustard Gas Mm.
0	18	...	754	0	75	0	0	0
16	17	772.5	901	129	91	21.3	162	328
19	18	772	924	152	93	24.0	182	368
22	20	771	954	183	95	26.6	202	409
40	18	768	1040	272	106	41.3	314	636
46	19	767	1092	325	111	48.0	365	738
72	25	764	1220	456	121	61.3	466	944
89	22	762	1183	421	121	61.3	466	944
96	24	761	1190	429	120	60.0	456	924
144	21	760	1088	328	110	46.6	354	716
187	20	767	1053	286	107	42.6	324	656

When the apparatus was disconnected, small amounts of hydrochloric acid gas and hydrogen sulfide were detected in the gases liberated by the action of sulfur monochloride on the β,β'-dichloroethyl sulfide. Owing to the solubility of hydrogen chloride in the latter substance, the increases in pressures shown in the tables and the accompanying plot do not actually represent the total gases produced.

CONCLUSIONS

1—There is a decided interaction when small amounts of sulfur monochloride are placed in contact with large amounts of β,β'-dichloroethyl sulfide.

2—This interaction is manifested by pressures resulting from the production of gases. The maximum pressure is reached at the end of 3 days.

3—A secondary reaction takes place between the substance and the gases, as indicated by a decrease in pressure at the end of three days.

THE SOLUBILITY OF β,β'-DICHLOROETHYL SULFIDE IN PETROLEUM HYDROCARBONS AND ITS PURIFICATION BY EXTRACTION WITH THESE SOLVENTS[1,2]

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The question of the solubility of dichloroethyl sulfide in petroleum hydrocarbons has been investigated for the purpose of ascertaining the suitability of such solvents as agents in extracting pure mustard gas from the crude commercial product. Its marked solubility in the common petroleum hydrocarbons was quite contrary to the belief commonly accepted in April 1918.

The method employed for the study of the intersolubility of dichloroethyl sulfide and the petroleum hydrocarbons was essentially that used by Rothmund.[1]

NATURE AND PREPARATION OF MATERIALS

DICHLOROETHYL SULFIDE—The material which was used in the intersolubility experiments was obtained by double distillation at a pressure of 13 to 14 mm.

PETROLEUM HYDROCARBONS—The ligroin utilized was obtained from the commercial material by distillation. Only that portion distilling below 100° was employed. The specific gravity of the distillate at 24° C. was 1.6677. The nature of the other hydrocarbons used is illustrated by the distillation curves shown in Fig. 1.

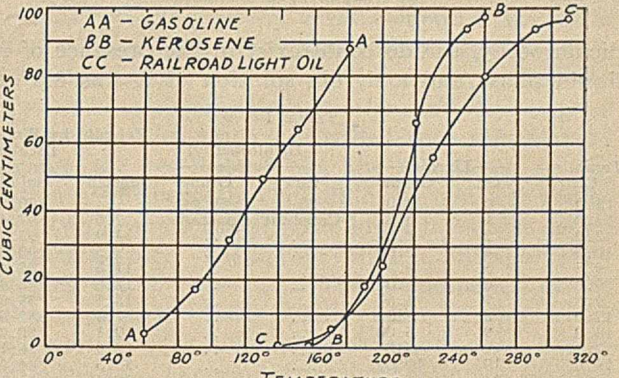

FIG. 1—DISTILLATION CURVES OF HYDROCARBONS USED

SULFUR MONOCHLORIDE—This was obtained by distillation of the commercial product, the portion boiling between 136° to 138° C. being utilized.

SULFUR—The pulverized C. P. rhombic modification was employed.

CHLORINATED MUSTARD GAS—This was made by the interaction of distilled dichloroethyl sulfide with sulfur dichloride in a carbon tetrachloride solution below 50° C. The addition of the dichloride solution was gradual and accompanied with constant shaking. When the product was distilled at 17 mm. pressure, the excess of sulfur dichloride and carbon tetrachloride distilled off first. The chlorinated product which came over at 112° was collected separately and used in the intersolubility experiments given in Table VI. It was of a light brown color, and its specific gravity at 22° was 1.355.

INTERSOLUBILITY EXPERIMENTS

DICHLOROETHYL SULFIDE AND LIGROIN—The results obtained from a study of the intersolubility of dichloroethyl sulfide and ligroin at various temperatures are given in Table I and illustrated by the curve AA in Fig. 2. The critical point of solubility, that is, the temperature above which the two substances would be mutually soluble in all proportions, was found to be 19° C. The highest temperature at which solid

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[1] Published by permission of the Chief of the Chemical Warfare Service.

[2] The authors wish to acknowledge the advice and suggestions given by Major Wm. Lloyd Evans and also the assistance received from Messrs. J. J. Alexander, J. H. Black, W. H. Gersdoroff, H. H. Harvey, Bruce Howard, J. L. Hutchinson, E. C. Mack, L. S. Minor, J. Parsons, G. T. Sohl, G. F. Seimers, M. C. Taylor, R. W. Tatem, D. R. Virtue, and C. J. Wernlund.

[1] *Z. physik. Chem.*, **26** (1898), 433.

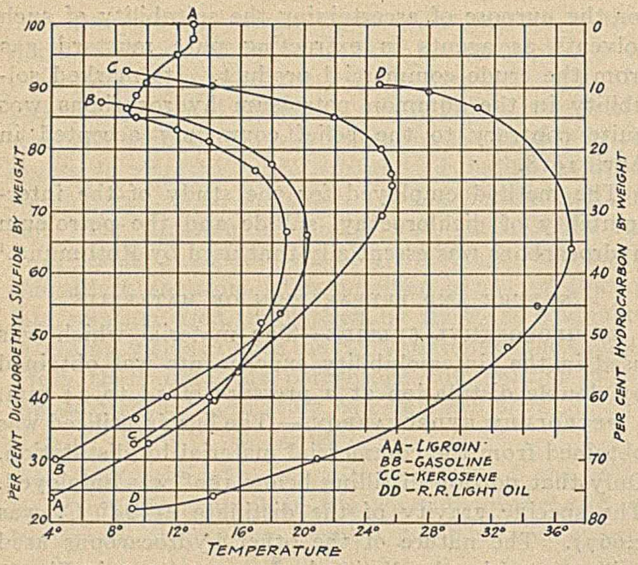

FIG. 2—INTERSOLUBILITY OF DICHLOROETHYL SULFIDE AND HYDROCARBON SOLVENTS

dichloroethyl sulfide could exist in the presence of its liquid phase and a ligroin solution of it was 8.8° C.

TABLE I

Temp. ° C.	Ligroin Cc.	Ligroin Grams	Dichloroethyl Sulfide Cc.	Dichloroethyl Sulfide Grams	Per cent by Weight Ligroin	Per cent by Weight Dichloroethyl Sulfide
13.0	0	0.00	20	25.44	..	100.0
13.0	1	0.67	Constant	Constant	2.6	97.4
12.0	2	1.34	...	..	4.9	95.1
10.0	4	2.67	...	..	9.5	90.5
9.5	5	3.34	...	..	11.6	88.4
9.0	6	4.00	...	..	13.6	86.4
9.6	7	4.67	...	..	15.5	84.5
12.0	8	5.34	...	..	17.4	82.6
14.0	9	6.00	...	..	19.1	80.9
17.22	12	8.01	...	..	23.9	76.1
19.0	19	12.69	...	..	33.3	66.7
19.0	24	16.03	...	..	38.6	61.4
18.3	29	19.36	...	..	43.2	56.8
17.5	39	26.04	...	..	50.6	49.4
16.0	49	32.72	...	..	56.3	43.7
14.5	59	39.39	...	..	60.7	39.3
10.3	79	52.75	...	..	67.5	32.5
6.5	99	66.10	...	..	72.2	27.8
2.5	119	79.46	...	..	75.8	24.2
0.2	30	20.03	3.0	3.82	83.9	16.1
—2.5	Constant	Constant	2.5	3.18	86.3	13.7
—6.5	...	...	2.0	2.54	88.7	11.3
—7.5	...	...	1.5	1.91	91.3	8.7

DICHLOROETHYL SULFIDE AND GASOLINE—The critical temperature of solubility of dichloroethyl sulfide was found to be 20.4°. The data obtained from these experiments are given in Table II and illustrated by the curve BB in Fig. 2.

TABLE II

Temp. ° C.	Dichloroethyl Sulfide Cc.	Dichloroethyl Sulfide Grams	Gasoline Cc.	Gasoline Grams	Per cent by Weight Dichloroethyl Sulfide	Per cent by Weight Gasoline
7.3	20.05	25.43	5.00	3.686	87.34	12.66
18.0	Constant	Constant	10.00	7.371	77.53	22.47
20.4	...	...	17.75	13.095	66.02	33.98
18.7	...	...	30.00	22.113	53.49	46.51
14.0	...	...	40.00	29.484	46.32	53.68
9.5	...	...	60.00	44.226	36.51	63.49
4.5	...	...	80.00	58.968	30.14	69.86
7.8	15.00	19.03	3.80	2.801	87.17	12.83
13.5	Constant	Constant	30.05	22.150	46.21	53.79
9.0	...	...	45.00	33.170	36.46	63.54
4.2	...	...	60.00	44.226	30.08	69.92

DICHLOROETHYL SULFIDE AND KEROSENE—Table III shows the results secured from the study of the mutual solubilities of dichloroethyl sulfide and kerosene at various temperatures. These determinations indicate that the critical point of solubility of dichloroethyl sulfide and kerosene is 25.6°. The data given in Table III are illustrated in Fig. 2 by the curve CC.

TABLE III

Temp. ° C.	Kerosene Cc.	Kerosene Grams	Dichloroethyl Sulfide Cc.	Dichloroethyl Sulfide Grams	Per cent by Weight Kerosene	Per cent by Weight Dichloroethyl Sulfide
14.2	60	48.24	25.0	31.88	60.21	39.79
9.5	80	64.32	25.0	31.88	66.87	33.13
21.9	7	5.63	25.0	31.88	15.07	84.93
24.3	9	7.23	25.0	31.88	18.58	81.42
25.6	12	9.65	25.0	31.88	23.33	76.67
25.6	13	10.45	25.0	31.88	24.79	75.21
25.6	14	11.26	25.0	31.88	26.20	73.80
25.0	18	14.47	25.0	31.72	31.33	68.67
14.3	6	4.82	33.0	41.88	10.32	89.68
8.9	6	4.82	43.0	54.47	8.12	91.88

DICHLOROETHYL SULFIDE AND RAILROAD LIGHT OIL—The results secured in these experiments are shown in Table IV and illustrated by the curve DD in Fig. 2. The critical point of solubility was found to be 37°.

TABLE IV

Temp. ° C.	Railroad Light Oil Cc.	Railroad Light Oil Grams	Dichloroethyl Sulfide Cc.	Dichloroethyl Sulfide Grams	Railroad Light Oil	Dichloroethyl Sulfide
25.0	2.45	1.926	14.95	18.966	9.22	90.78
28.0	5.12	4.024	25.00	31.715	11.26	88.74
31.3	3.74	2.940	14.95	18.966	13.42	86.58
37.0	13.69	10.760	Constant	Constant	36.20	63.80
35.0	20.19	15.869	...	....	45.52	54.48
33.0	26.19	20.585	...	....	52.05	47.95
23.6	38.57	30.316	...	....	61.51	38.49
20.9	56.62	44.503	...	....	70.12	29.88
14.5	75.07	59.005	...	....	75.67	24.33
9.3	87.42	68.692	...	....	78.36	21.64

From these results it is evident that with the increase in the percentage of high boiling hydrocarbons, the critical temperature of solubility for these solvents and dichloroethyl sulfide will also increase. This is very nicely illustrated by a comparison of the solubility curves shown in Fig. 2.

SOLUBILITY OF SULFUR MONOCHLORIDE IN THE HYDROCARBONS—Sulfur monochloride was found to be soluble in all proportions in ligroin, gasoline, kerosene, and railroad light oil at temperatures above 0°.

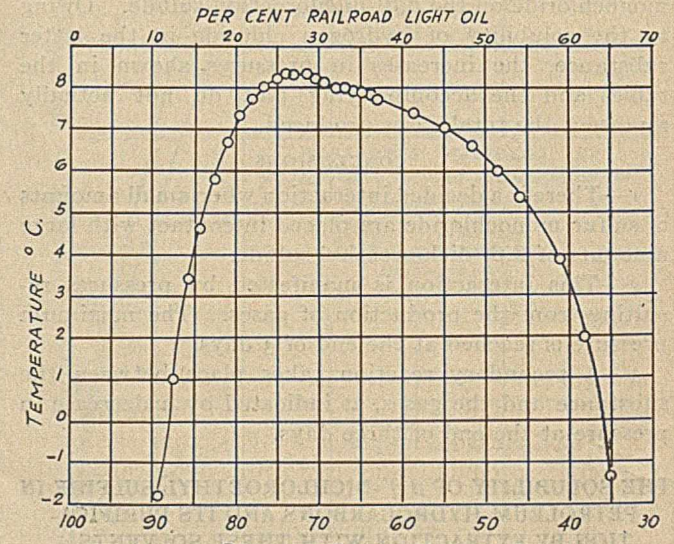

FIG. 3—INTERSOLUBILITY OF CHLORINATED MUSTARD GAS AND RAILROAD LIGHT OIL

SOLUBILITY OF SULFUR IN LIGROIN—Ligroin was shaken with powdered rhombic sulfur at 0° and at room temperature for about 6 hrs. The excess of sulfur was removed by rapid filtration. Twenty-five cc. of the filtrates were pipetted into a weighed dish and the solvent evaporated, with the results given in Table V.

TABLE V

Temp. ° C.	Sulfur in 25 Cc. Ligroin Gram	Correction (Blank)	Corrected Weight	Sulfur in 100 Cc. Ligroin Gram
0	0.049	0.001	0.048	0.192
0	0.052	0.001	0.051	0.204
24	0.085	0.001	0.084	0.336
24	0.080	0.001	0.079	0.316
24.5	0.081	0.001	0.081	0.324
28	0.092	0.001	0.091	0.364

INTERSOLUBILITY OF CHLORINATED MUSTARD GAS AND RAILROAD LIGHT OIL—The critical temperature of solubility of chlorinated mustard gas and railroad light oil was found to be 8.3°. The data obtained in these experiments are given in Table VI and illustrated in Fig. 3.

TABLE VI

Temp. ° C.	Railroad Light Oil Cc.	Railroad Light Oil Grams	Chlorinated Mustard Gas Grams	Per cent by Weight Railroad Light Oil	Per cent by Weight Chlorinated Mustard Gas
...	0	0.000	33.793	0.00	100.00
...	1	0.791	Constant	2.28	97.72
Below —2	2	1.582	....	4.47	95.53
Below —2	3	2.373	....	5.65	93.44
Below —2	4	3.164	....	8.56	91.44
—1.8	5	3.955	....	10.58	89.72
1.0	6	4.74	....	12.42	87.58
3.3	7	5.53	....	14.08	89.92
4.7	8	6.33	....	15.78	84.22
5.8	9	7.11	....	17.48	82.52
6.7	10	7.91	....	18.98	81.02
7.3	11	8.70	....	20.58	79.42
7.7	12	9.49	....	21.92	78.08
8.0	13	10.29	....	23.35	76.65
8.2	14	11.08	....	24.69	75.30
8.3	15	11.87	....	25.99	74.01
8.3	16	12.67	....	27.27	72.73
8.3	17	13.47	....	28.51	71.49
8.2	18	14.23	....	29.63	70.37
8.1	19	15.02	....	30.77	69.23
8.0	20	15.81	....	31.87	68.13
7.95	21	16.60	....	32.94	67.06
7.90	22	17.39	....	33.97	66.03
7.85	23	18.18	....	34.98	65.02
7.80	24	18.97	....	35.95	64.05
7.7	25	19.76	....	36.89	63.11
7.35	30	23.73	....	41.25	58.75
7.0	35	26.78	....	45.02	54.98
6.6	40	31.63	....	48.34	51.66
6.0	45	35.58	....	51.32	48.68
5.35	50	39.53	....	53.90	46.10
3.85	60	47.46	....	58.41	41.59
2.0	70	55.37	....	62.09	37.91
—1.4	80	63.28	....	65.18	34.82
Below —2	90	71.19	....	67.80	33.20

CONCLUSIONS FROM SOLUBILITY EXPERIMENTS

1—Dichloroethyl sulfide is soluble in the petroleum hydrocarbons and there is complete miscibility of the solute and solvent at relatively low temperatures.

2—Sulfur monochloride is soluble in all proportions.

3—Only a small amount of sulfur dissolves in the petroleum hydrocarbons.

4—Chlorinated mustard gas is soluble in all proportions of railroad light oil above 8.8°.

APPLICATION OF RESULTS—As the result of the data given above, it is self-evident that it would be highly desirable to take advantage of the following facts in a method of extracting mustard gas from the crude commercial product, using petroleum hydrocarbons as solvents.

(1) Extract the crude mustard gas at a temperature slightly above the critical point of solubility. Most of the sulfur, together with a tar-like mass, will remain insoluble.

(2) The supernatant solution is cooled considerably below the critical temperature, causing the formation of two liquid layers, the lower layer being primarily a solution of the hydrocarbon in the mustard gas. If the temperature be sufficiently lowered, solid mustard gas will precipitate out from the solution. This solid mass will retain a little of the hydrocarbon.

(3) The upper layer of hydrocarbon solvent, or that above the solid material, will contain all traces of sulfur monochloride together with chlorinated products of dichloroethyl sulfide in the crude mustard gas, and also certain amounts of dichloroethyl sulfide. The concentration of the latter will be a function of the temperature. This solvent may be used until the percentage of products other than dichloroethyl sulfide makes it undesirable.

(4) The lower layer will contain dichloroethyl sulfide and certain amounts of the hydrocarbon, the percentage of the latter being a function of the temperature.

SINGLE EXTRACTION

In order to demonstrate that such a separation as described below could be carried out, 200 cc. of crude mustard gas were shaken thoroughly with 200 cc. of ligroin in a separatory funnel at a temperature of 44° C. The mixture was allowed to cool very slowly to 25°. Three well-defined layers separated. The heaviest one consisted of a pitchy mass composed largely of sulfur. The second layer, a solution of ligroin in dichloroethyl sulfide, was drawn off in three portions and analyzed by weighing each portion and distilling off the ligroin. The amount distilled was obtained by weighing the residue. When the top layer, or the solution of dichloroethyl sulfide in ligroin, was cooled to 8°, two layers formed. The lower layer was drawn off and analyzed. The ligroin solution, or upper layer, was then cooled to —10°. The dichloroethyl sulfide precipitated in the form of long, white needles, which upon melting gave a light yellow solution containing a little sulfur. The results obtained from the analyses of the layers containing the ligroin in a solution of dichloroethyl sulfide are given in Table VII.

TABLE VII

Total Wt. of Layer Grams	Temp. of Layer ° C.	Weight Ligroin Dissolved Grams	Weight of Purified Dichloroethyl Sulfide Grams	Per cent	Melting Point ° C.	Remarks
14.8	25	0.3	14.5	5.4	..	Pitchy mass (S)
66.3	25	8.7	57.6	21.6	5.6	Dark yellow
65.2	25	8.5	56.7	21.2	4.6	Dark yellow
26.1	25	3.75	22.35	8.4	5.0	Dark yellow
80.35	8	11.05	69.3	26.0	9.0	Light yellow
59.8	—10	23.50	36.3	13.6	12.5	Light yellow

SUCCESSIVE EXTRACTION[1]

In this process a series of superimposed funnels was used. A diagram of the apparatus is shown in Fig. 4. The general method of procedure was to place equal volumes of ligroin (200 cc.) in each of the funnels. An equal volume of crude dichloroethyl sulfide (200 cc.) was then introduced in the top funnel. The contents of the first funnel were shaken, and the insoluble material which settled out from the ligroin layer was passed into Funnel 2. This passage was slow, drop by drop. As the drops came in contact with the ligroin layer in Funnel 2, they broke up into a fine spray, which scattered throughout the ligroin. The process was repeated in the succeeding funnels. Two

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[1] As the result of a large number of experiments with hydrocarbon solutions of mustard gas, it was noticed that the toxicity of these solutions appeared to be greater than that of either the commercial or pure mustard gas. This matter was called to the attention of the Research Division in June 1918.

experiments, illustrating the general results obtained by this process of extraction, gave 76.5 and 80.9 per cent of ligroin-soluble material. This soluble material was distilled *in vacuo* (2.0 to 5.0 mm.), and a yield of 86.98 per cent was obtained which showed a purity of 99.5 per cent (m. p. 13.75° C.). Better purification resulted from keeping the temperature of extraction a little below the critical point of solubility of the ligroin and dichloroethyl sulfide.

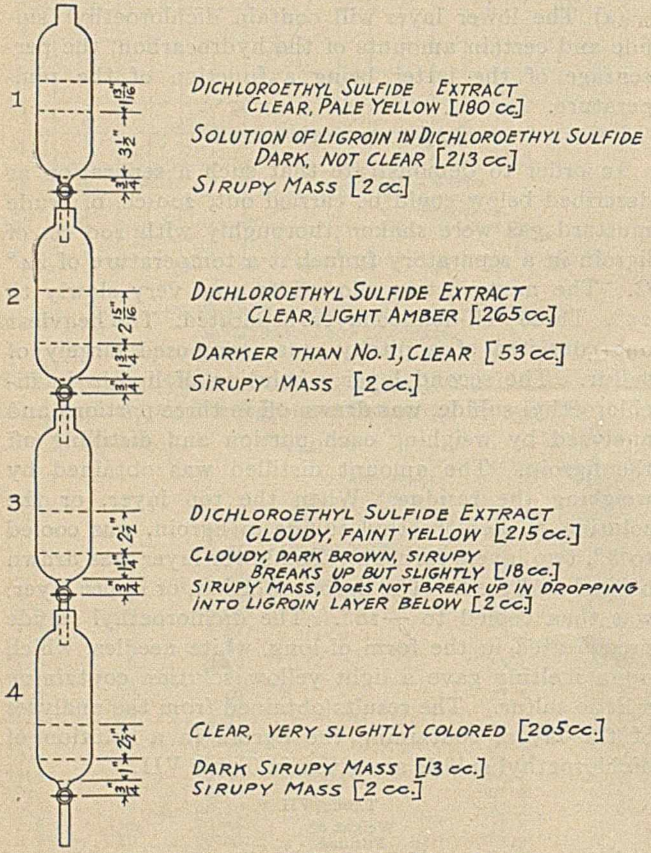

FIG. 4—SUCCESSIVE EXTRACTION APPARATUS

The ligroin solutions when cooled to —10° gave beautiful, long, white needles, which were permitted to melt slowly after decantation of the mother liquor. Upon melting, two layers were obtained, the upper layer consisting largely of the ligroin that had been retained mechanically by the crystals. A very good product was obtained in yields varying from 51 to 63 per cent, depending upon the extent of concentration and degree of extraction. This dichloroethyl sulfide had melting points which varied from 10.4° to 10.8° C.

In all cases of extraction it was very difficult to remove the last traces of ligroin. A small amount of the hydrocarbon caused a considerable lowering of the freezing point. To determine the actual amounts of dichloroethyl sulfide contained in the various samples, distillation gave by far the more accurate results.

INSOLUBLE RESIDUE—This insoluble layer obtained from the fourth funnel in the successive extraction experiments was a thick sirupy mass and contained only traces of mustard gas. While the residues were not subjected to distillation, there was very good evidence that only very small amounts of mustard gas were present. This is found in the fact that the mustard gas dissolved in the ligroin and *vice versa*, and only a very small amount of ligroin is found in the insoluble residue. Further, this insoluble mass consists largely of sulfur, and the mustard gas is only sparingly soluble in sulfur.

ANALYSIS OF CRUDE MUSTARD GAS

The analysis of crude mustard gas used in all experiments herein reported was made as follows:

A measured volume of crude material was placed in a distilling flask of 750 cc. capacity, and the flask attached to a condenser, which was connected with a weighed receiver, and the system evacuated. The distillations were made at a pressure of 6 to 13 mm. Upon heating the distilling flask, and before any distillate was collected, there was a decided evolution of gas. While the last portion of the mustard gas was being distilled there was considerable bumping and frothing, and great care had to be manifested in completing the work. The distillate was light lemon-yellow in color. The black residue in the flask contained quantities of sulfur, was insoluble in ligroin, and dissolved in carbon tetrachloride. Table VIII gives the results obtained in two analyses.

TABLE VIII

	Sample No. 1	Sample No. 2
Weight, grams	399	261
Volume, cc.	300	200
Weight of distillate, grams	295.8	194.7
Per cent	74.17	74.6
Volume of distillate, cc.	233	157
Per cent	77.7	78.5
Weight of residue, grams	98.6	60.7
Per cent	24.65	23.3
Volatile, grams	4.6	5.6
Per cent	1.2	2.2
Freezing point of distillate, ° C.	12.0	12.7
Purity, per cent	94.2	96.5
Percentage pure mustard gas	69.9	72.0
Average Percentage	71.0	

ANALYSIS OF CRYSTALS OF DICHLOROETHYL SULFIDE OBTAINED FROM LIGROIN SOLUTION

After removing as much as possible of the ligroin retained by the crystals, they were weighed out and subjected to distillation, the results being as follows:

TABLE IX

Weight of sample, grams	313.1
Melting point, ° C.	7.4
Weight of distillate, grams	278.9
Melting point, ° C.	13.7
Purity of distillate, per cent	99.3
Per cent mustard gas in sample	89.08
Weight of residue, grams	25.7
Per cent	8.2
Weight of ligroin (by difference), grams	8.5
Per cent	2.7
Calculated as ligroin-free:	
Per cent mustard gas	90.92
Per cent residue	9.08

CONTINUOUS EXTRACTION

METHOD AND APPARATUS—In order to have a continuous process for the extraction of mustard gas from the crude material by means of ligroin, the apparatus shown in Fig. 5 was devised. The crude material flows from a separatory funnel into the main portion of the apparatus, which consists of a glass tube, about 4 ft. in length, with a bulb blown at the upper end, which serves as a settling chamber, and a stopcock at the lower end, which permits the removal of the insoluble matter. The ligroin is introduced into the apparatus by means of a long glass tube, sealed into the side of the glass column about 6 in. from the bottom. At the start the main portion of the apparatus is nearly filled with ligroin. The crude material, which enters the apparatus just below the settling chamber, is sprayed through the column of ligroin. The insoluble matter settles slowly to the bottom of the tube. Almost complete extraction should be assured, for as the mass settles toward the bottom, it comes in contact with the fresh ligroin. The overflow outlet, near the top of the apparatus, consists of a tube sealed into the long glass column and bent downward at right angles so that the liquid will flow into a container placed under it. A large separatory funnel is utilized for the collection of the ligroin solution from the overflow tube. When this funnel is nearly filled it is removed and placed in a cooling bath. The insoluble matter collecting at the bottom of the apparatus is drawn off from time to time into a graduated cylinder.

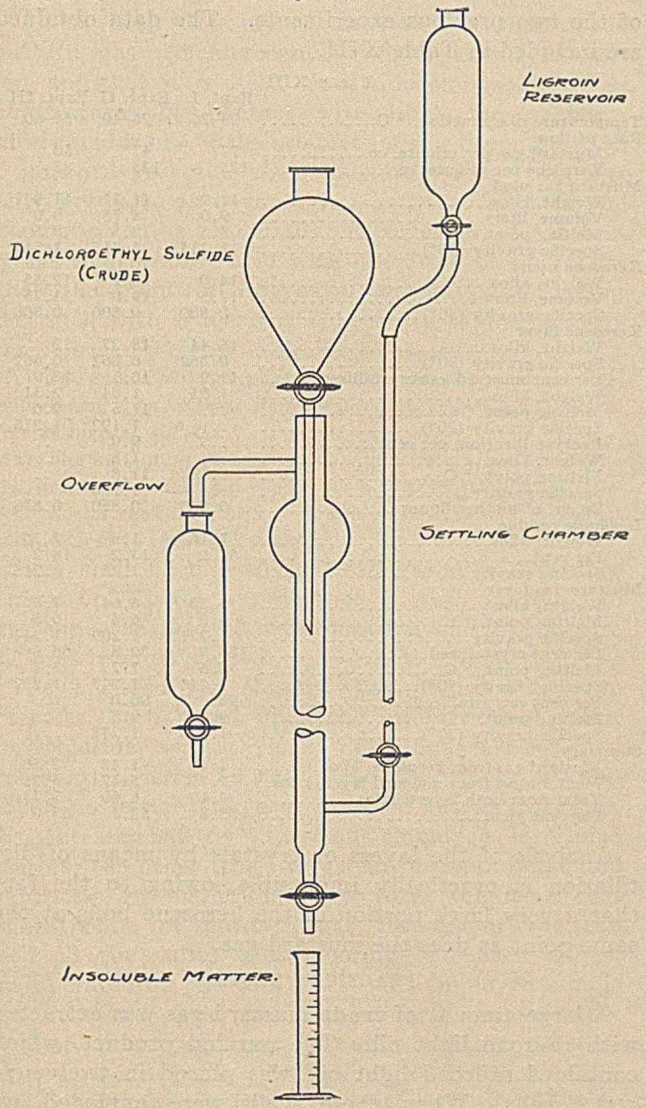

Fig. 5—Continuous Extraction Apparatus

EXPT. I. ABOVE THE CRITICAL POINT OF SOLUBILITY—Measured volumes of crude mustard gas and of ligroin were placed in their respective reservoirs, and the extraction carried out as described above, at temperatures varying from 25° to 27°, or several degrees above the critical point of solubility. The data are given in Table X.

Table X

Volume of ligroin used, cc.	1800
Volume accounted for, cc.	1713
Volume of crude mustard gas used, cc.	800
Volume accounted for, cc.	796
Insoluble matter at extraction temperature	
Weight, per cent	13.5
Volume, per cent	12.3
Insoluble matter at 16° to 18°	
Weight, per cent	17.4
Volume, per cent	17.9
Mustard gas crystallized	
Weight, per cent	43.7
Volume, per cent	45.4
Dissolved material in mother liquor	
Weight, per cent	22.7
Volume,,per cent	24.0

EXPT. II. BELOW THE CRITICAL POINT OF SOLUBILITY—Eight hundred cc. of crude mustard gas were run through the ligroin at 15° in the continuous extraction apparatus. The insoluble matter drawn off at the bottom of the apparatus measured 745 cc. A large portion of this was ligroin which had been dissolved by the insoluble material. This residue was passed through the apparatus four times. Proper regulation of flow possibly would have increased the efficiency of extraction. The ligroin solution was placed in the freezing bath, and the mother liquor from the crystals of mustard gas was utilized in further extraction of the insoluble matter. The results obtained are given in Table XI. The weight of the insoluble matter was calculated from the data obtained in the previous experiment. It will be noted that the insoluble matter at extraction temperature in Expt. I, together with the insoluble matter at 16° to 18°, gave a total volume of 308 cc. and weighed 332 g. After the fourth extraction in this experiment (Table XI). the total insoluble material was 290 cc.

Table XI

Volume of ligroin used, cc.	1200
Volume of crude mustard gas, cc.	800
Weight of crude mustard gas, grams	1068.8
Volume of mother liquor (does not include that retained by insolubles and crystals), cc.	900
Insoluble matter, per cent	36.3
Mustard gas frozen from ligroin, per cent	51.6
Material retained by mother liquors (by difference), per cent	12.1

A portion of the mustard gas frozen out from the ligroin solution was taken for analysis after a large part of the mechanically retained ligroin had been removed by distillation. This product was distilled in a vacuum of about 13 mm., thus removing the ligroin still present. The oil bath was heated gently to 80°, and then to 95° to 100°. The data in Table XII were obtained as the result of this analysis.

Table XII

Weight of sample, grams	311.2
Weight of distillate, grams	277.8
Melting point, ° C.	13.7
Purity of distillate, per cent	99.3
Per cent of mustard gas in sample	88.64
Weight of residue, grams	25.1
Per cent	8.0
Weight of ligroin (by difference), grams	10.2
Per cent	3.4
Per cent mustard gas (calculated on ligroin-free sample)	92.2

CONTINUOUS EXTRACTION OF CRUDE MUSTARD GAS WITH KEROSENE AND RAILROAD LIGHT OIL ON A SEMI-COMMERCIAL SCALE

The object of the following experiments was to confirm the results of those carried out in glass apparatus on a laboratory scale and at the same time to simulate as closely as possible the conditions which would obtain in plant operation. The crude mustard gas was manufactured at the Edgewood Plant of Edgewood Arsenal on August 29, 1918. It had a melting point of 8.5°, was black in color, and on analysis by distillation showed 70 per cent pure mustard gas.

APPARATUS AND METHODS—To minimize danger as much as possible the apparatus was set up in an improvised laboratory out of doors. The extractor was an all-lead column with a brass valve at the bottom, and of the same essential design as the glass extractor. Its principal parts consisted of a 1.5 in. (inside diameter) lead pipe, with enlarged sections at the top and the bottom. These sections were used as settling chambers and gave the apparatus proper a length of 4 ft. A three-eighths inch vertical pipe, attached just above the lower settling chamber, was of sufficient length to furnish a pressure head which would cause a counter current to flow through the apparatus when in operation. The crude mustard gas was admitted through another vertical lead pipe entering at the top of the upper settling chamber and terminating at the center of the 1.5 in. lead pipe, about 2 in. below the bottom of the settling chamber. A three-eighths inch heating pipe, through which steam was passed when extracting at a higher temperature, ran throughout the length of the apparatus. A thermometer well was placed in the top of the apparatus in order to measure the temperature of the effluent as it left the overflow pipe. The apparatus had a volume of 7.5 liters. The accessories, such as containers, funnels, crystallizing vessels, etc., were of glass.

The extractor was operated by running about 4 liters of kerosene into the apparatus. The kerosene supply was then turned off and the material to be extracted was run in at a definite rate of flow. As soon as the extract came through the overflow pipe, the kerosene was again permitted to flow through the apparatus. The insoluble matter was drawn off at the bottom of the extractor from time to time.

EXPT. I—This and the following experiments were carried out in much the same manner as already described for continuous extraction.

The extract and the insoluble residue were run into tared bottles, and weighed. The bottle containing the extract was refrigerated at about —15° for 3 hrs., after which time large needle-like crystals formed a compact mass throughout the liquid. During the refrigeration two liquid phases settled out, the lower one black in color and very rich in mustard gas, and the upper orange in color and low in its mustard-gas content. The crystals were permitted to melt and the two liquid layers which formed were separated and weighed. Each layer was refrigerated as before and the remaining liquid drained from the crystals, the weights of which were determined. A second, third, and fourth fraction of crystals were obtained from the lower layer on further crystallization. The upper, or kerosene layer, yielded only one fraction. In draining off the mother liquor from the crystals the bottles were simply held in an inverted position for a few minutes. The data are given in Table XIII.

EXPT. II—This experiment differed from Expt. I in that the rate of flow of mustard gas was slower in order to insure more complete extraction. The results are given in Table XIII.

EXPT. III—This experiment was exactly like Expt. I, excepting that the rates of flow of the crude mustard gas and the kerosene were much slower, and the temperature of extraction was higher. The kerosene used in this experiment was obtained from the mother liquors of the two previous experiments. The data obtained are included in Table XIII.

TABLE XIII

	Expt. I	Expt. II	Expt. III
Temperature of extraction, ° C.	23–26	26–40	50–60
Rate of flow			
Mustard gas per minute, cc.	77	47	50
Kerosene per minute, cc.	125	125	83
Mustard gas used			
Weight, kilos	11.9	11.5	11.9
Volume, liters	9.0	8.75	9.0
Melting point, ° C.	8.5	8.5	8.5
Specific gravity (30°)	1.315	1.315	1.315
Kerosene used			
Weight, kilos	14.0	15.2	12.55
Volume, liters	17.5	19.0	14.75
Specific gravity (30°)	0.800	0.800	0.800
Kerosene layer			
Weight, kilos	16.44	18.27	12
Specific gravity (30°)	0.862	0.862	0.862
Per cent mustard gas crystallized	11.9	10.1	18.9
Weight, kilos	1.95	1.84	2.31
Melting point, ° C.	...	11.6	9.6
Specific gravity (20°)	...	1.192	1.216
Recrystallization, per cent	...	9.9	..
Weight, kilos	...	1.8	..
Melting point, ° C.	...	11.8	..
Specific gravity	...	1.210	..
Sp. gr. of mother liquor	0.850	0.850	0.870
Insoluble residue			
Weight, kilos	7.16	1.5	2.16
Per cent	61.2	13.2	18.2
Specific gravity (20°)	...	1.251	1.246
Mustard gas layer			
Weight, kilos	3.30	6.64	7.66
Melting point, ° C.	6.6	6.3	6.5
Specific gravity	1.221	1.209	1.244
Per cent crystallized	84.3	82.5	68.3
Melting point, ° C.	8.6	7.7	7.1
Specific gravity (20°)	1.244	1.247	1.252
Per cent recrystallized	98.4	96.0	..
Melting point, ° C.	9.5	9.5	..
Specific gravity (20°)	1.246	1.248	..
Summary			
Mustard gas from kerosene, kilos	1.40	1.13	2.50
Mustard gas from mustard layer, kilos	2.79	5.47	5.23
Total from both layers, kilos	4.19	6.60	7.73
Per cent yield	35.8	58.1	65.0

Analysis of the layers or crystals by means of distillation is practically impossible, owing to the fact that a very large portion of the kerosene boils at the same point as does the mustard gas.

PRACTICAL TESTS

A large amount of crude mustard gas was extracted with railroad light oil. The purified product, which contained railroad light oil, was placed in twelve 75 mm. shells. When these shells were exploded no flash resulted, showing that the hydrocarbon did not take fire. At the time of explosion a white cloud of smoke was produced.

CONCLUSIONS

1—The critical temperatures of solubility of dichloroethyl sulfide with the various hydrocarbons are as follows:

Ligroin	19°
Gasoline	20.4°
Kerosene	25.6°
Railroad Light Oil	37°

2—The critical temperature of solubility increases with the increase in the percentage of the more complex hydrocarbons.

3—The critical temperature of solubility of chloromustard gas is considerably below that of dichloroethyl sulfide.

4—Dichloroethyl sulfide can be extracted from the crude material, containing 71 per cent, to give yields varying from 54 per cent to 69 per cent.

DECOMPOSITION OF AND PRESSURE DEVELOPED BY MUSTARD GAS IN STEEL SHELL AT 60° C.[1]

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It has been determined qualitatively that crude mustard gas (dichloroethyl sulfide) slowly attacks iron, and that it is itself slowly decomposed at room temperatures by contact with iron. Since hydrochloric acid is one of the products of this decomposition of mustard gas, and since mustard gas as commercially produced is never quite dry, the effect of the decomposition is essentially a corrosion of the iron by the hydrochloric acid with liberation of hydrogen. Since the plant of Edgewood Arsenal was loading steel shell with crude mustard gas for shipment overseas, it became highly desirable to ascertain:

(1) The extent of decomposition of the mustard gas in the steel shells during a two weeks' journey in cargo vessels, at temperatures as high as 50° C.

(2) The maximum pressure that would obtain inside of the shell, in order to make provisions for a sufficiently tight or leak-proof booster-shelljoint, and to provide boosters with sufficient wallthickness to prevent caving in.

Steel shell filled with mustard gas were therefore kept at 60° C. for a period of 2 wks., in order to determine the rate of decomposition and to measure the pressures developed.

The mustard gas shipped was prepared by two processes, both based upon the interaction of sulfur monochloride and ethylene. The one (the original process, designated in this paper as Process A) employed no initial charge of mustard gas as catalyzer, was operated at 60° C., and employed lead-lined reactors; the other (the Levinstein process, designated as Process B) maintained a 70 to 75 weight per cent concentration of mustard gas throughout the run until all the sulfur monochloride had been added, was operated at 30° to 35° C., and employed simple iron reactors. The products differed considerably in color, purity, amount of sulfur held in colloidal solution, acidity, etc. Both kinds of crude mustard were investigated. The vast majority of the gas, however, was prepared according to Process B.

METHODS OF INVESTIGATION

In order to gain information on the two points stated in the beginning of this paper, two series of experiments were made. The methods may be outlined as follows:

SERIES 1—Three hundred cc. samples of analyzed crude Process A and Process B mustard gas were placed in several 75 mm. shell. The shell were tightly closed by means of rubber stoppers and were kept in a thermostat at 60° C. (±1°) for a period of 16 days for the Process B samples, and 8 days for the Process A samples. A test sample was taken every two days in the order of shell number, two successive samples being taken from each shell. Two shell contained crude Process A and four shell Process B mustard gas, both of excellent quality initially. To detect any abnormal behavior during the testing period, a final sample was taken from each of the first four shell at the end of 16 days for the determination of acidity and final melting point.

SERIES 2—Three hundred cc. samples of analyzed crude Process B mustard gas were placed in 75 mm. shell connected with mercury manometers. Also, samples of Process B mustard gas which had been treated with gaseous ammonia (this procedure precipitating out about 7 to 8 per cent of the colloidal sulfur and destroying the HCl per cent) and of Process A mustard gas in which gas oil had been substituted for colloidal sulfur (by the process of extraction) were also placed in shell similarly arranged. As a check, samples of each material were placed in glass containers, producing the same void as in the steel shell, and connected to mercury manometers.

Table I—Progressive Decomposition of Mustard Gas in Steel Shell

Sample	Shell No.	Days in Shell	Melting Point (Crude) ° C.	Melting Point Lowering (Crude) ° C.	Relative Purity of Mustard Gas. Per cent	Drop in Percentage Purity	Per cent Acidity as HCl	Increase in Acidity
Process B	..	0	8.00	....	81.8	...	0.160	...
	1	2	7.90	—0.10	81.5	0.3	0.180	0.020
	1	4	7.50	—0.50	80.3	1.5	0.382	0.222
	2	6	7.20	—0.80	79.4	2.4	0.417	0.257
	2	8	7.05	—0.95	79.0	2.8	0.639	0.479
	3	10	7.10	—0.90	79.1	2.7	0.910	0.750
	3	12	6.95	—1.05	78.7	3.1	0.645	0.485
	4	14	6.10	—1.90	76.1	5.7	1.387	1.227
	4	16	6.00	—2.00	75.7	6.1	1.535	1.375
Process A	..	0	10.30	....	88.9	...	0.270	...
	5	2	9.40	—0.90	86.1	2.8	1.028	0.758
	5	4	9.20	—1.10	85.5	3.4	1.308	1.038
	6	6	9.60	—0.70	86.8	2.1	0.968	0.698
	6	8	9.40	—0.90	86.1	2.8	1.009	0.739

Zero readings were taken on each manometer at 30° C., the temperature of the bath when the manometers were sealed on. All connections had been tested for leaks. The temperature of the thermostat was raised to 60° C. and maintained at this temperature (± 1° C.) for over 10 days. An initial pressure reading was made one hour after the thermostat had been adjusted to 60° C. Subsequent manometer readings were made twice daily (at 8:30 A.M. and 4:30 P.M.).

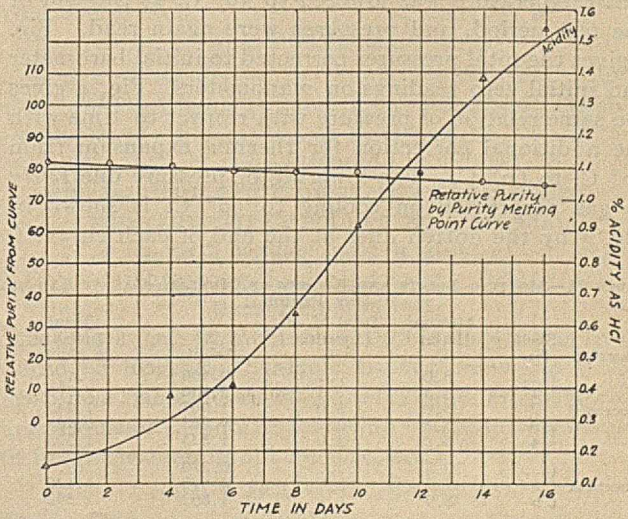

Fig. 1—Relative Purity and Acidity as a Function of Time

METHODS OF ANALYSIS

The tests for the determination of the progressive decomposition consisted of vacuum distillations, melting-point determinations on the crude and the distilled

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[1] Published by permission of the Chief of the Chemical Warfare Service.

samples, and acidity determinations. The percentage purity of the distilled product and the relative percentage purity of the crude were gaged by an empirically determined purity-melting point relation.[1] Acidity determinations were made by adding chloroform (to dissolve the mustard gas) and water, and titrating with a standardized sodium hydroxide solution.

In Series 2, melting-point, acidity, and purity tests were made only at the beginning and at the end of the 10-day period.

TABULATION OF RESULTS

The results obtained in Series 1 are presented in Tables I and II; in Fig. 1 are presented the melting-point lowerings and acidity increases as related to time in days, and in Fig. 2 the relation of melting-point lowering to acidity increase. The results of the analysis of initial and final materials of the shell of Series 2 are presented in Table III. Net decomposition pressures were obtained by subtracting initial readings at 60° C. from final readings at 60° C. The thermostat temperature was lowered to 30° C. at the end of the test period, and pressures were again read. Fig. 3 gives the total pressures corrected to initial barometer and initial zero readings on manometers. Fig. 4 gives the same relation of pressure with respect to time with the additional correction for thermal expansion from 30° C. to 60° C. The lowering of pressure due *solely* to gas absorption on cooling to 30° C. is shown in Fig. 3 by the dotted lines at the end of each curve.

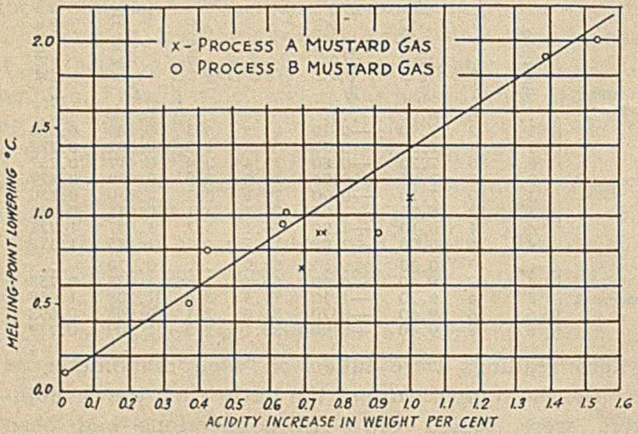

FIG. 2—MELTING-POINT LOWERING AS A FUNCTION OF ACIDITY INCREASE

TABLE II—MELTING POINTS AND ACIDITY OF MUSTARD GAS AT END OF 16-DAY PERIOD

SAMPLE	Shell No	Melting Point ° C.	Total M.-P. Lowering ° C.	Acidity	Total Increase in Acidity
Process B	..	8.0	...	0.160	...
	1	4.5	3.5	2.930	2.770
	2	5.0	3.0	1.907	1.747
	3	5.8	2.2	0.885	0.725
	4	6.0	2.0	1.535	1.375
Process A	..	10.3	...	0.270	...
	5	7.7	2.6	4.690	4.420
	6	8.9	1.4	1.862	1.592

Table II presents the results of determinations of the melting point and the acidity on the residual mustard gas in the shell of Series 1 at the end of 16 days.

TABLE III—ANALYSIS OF ORIGINAL AND FINAL MUSTARD GAS IN PRESSURE DEVELOPMENT TESTS (AT END OF 10 DAYS)

SAMPLE	Melting Point ° C.	Melting-Point Change	Relative Purity Per cent	Change in Purity	Per cent Acidity, as HCl	Increase in Acidity
Original Crude Process B	8.0	...	82.4	...	0.175	...
Process B from steel shell	6.4	—1.6	76.5	—5.9	2.040	1.865
Process B from glass container	7.6	—0.4	81.2	—1.2	0.456	0.281
Process B, ammonia-treated	8.1	...	82.7	...	0.005	...
Ammonia-treated, from shell	8.1	±0.0	82.7	±0.0	0.422	0.417
Ammonia-treated, from glass container	8.6	+0.5	84.4	+1.7	0.012	0.007
Original Sample Process A + 12 per cent oil	7.9	...	82.1	...	0.073	...
Process A + 12 per cent oil, from shell	7.2	—0.7	80.0	—2.1	0.661	0.588

DISCUSSION OF RESULTS

The data obtained in Series 1 offer substantial proof of a progressive decomposition of mustard gas in steel shell at temperatures near 60° C. This time-relative purity relation for Process B mustard gas is practically a linear function (see Fig. 1). The increase of acidity with time in the closed steel shell is also presented in the figure, showing practically a uniform rise. An increase in acidity goes hand in hand with a lowering of melting point and a decrease in actual mustard gas content. This is shown in Fig. 2.

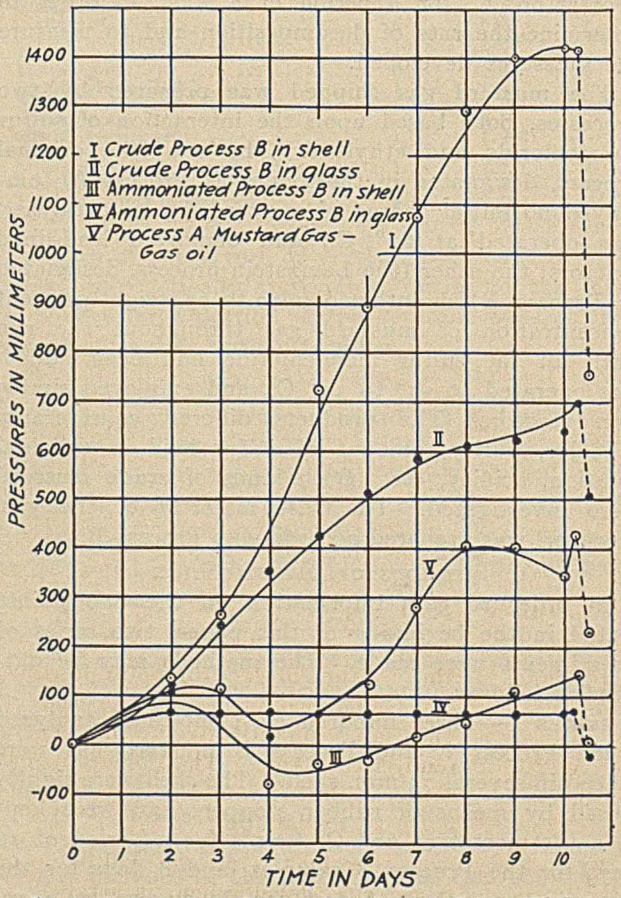

FIG. 3—DECOMPOSITION PRESSURE OF MUSTARD GAS AT 60° C. (Not Corrected for Thermal Change)

The Process A mustard gas tests were continued over a period of only 8 days, and though the results are not as concordant as those on Process B mustard gas, the decomposition and the increase in acidity proceed in the same general way as for Process B.

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[1] Bureau of Mines, *Organic Report* **28**, April 6, 1918.

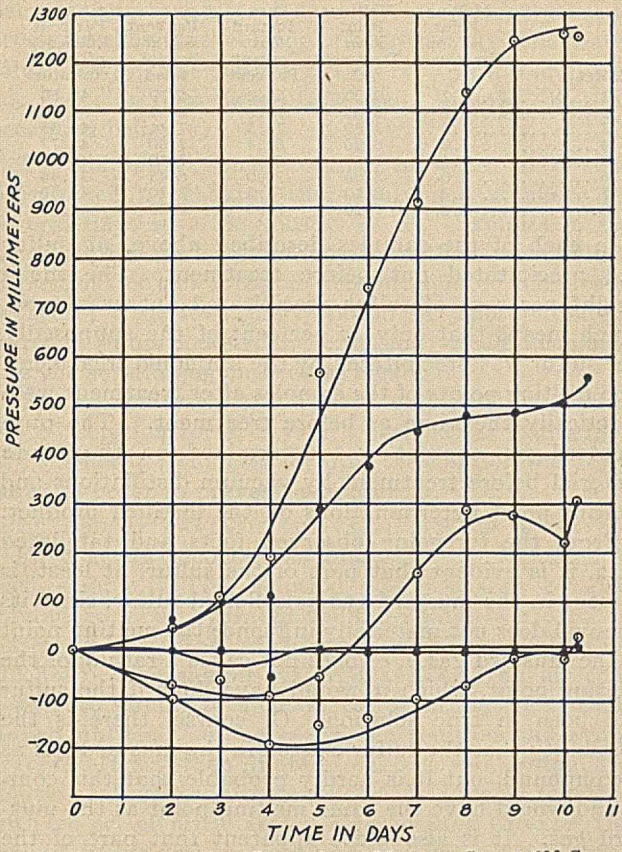

FIG. 4—DECOMPOSITION PRESSURE OF MUSTARD GAS AT 60° C.
(Corrected for Thermal Change)

Analysis by means of vacuum distillation does not yield satisfactory results, because the amount of sulfur precipitated out of colloidal solution varies with the time, and hence the analysis of the supernatant liquid is not a true criterion of the purity of the sample. Further, an actual decomposition of the mustard gas may be counterbalanced by a precipitation of sulfur, the precipitated sulfur adhering to the sides of the shell. The reliable criterion for determining the extent of decomposition was the melting-point determination on the undistilled mustard; since in this determination the colloidal sulfur does not affect the melting point, while the decomposition products do. Hence, a relative purity based upon these melting points is recorded, and the results given graphically in Fig. 1.

In Series 2, the relation of melting-point lowering and total acidity is again confirmed; while the relation is not the same quantitatively, the general behavior and trend is the same. The deviation may be due to several causes, but it would be idle curiosity to attempt to make an explanation.

By reference to either Figs. 3 or 4, it will be noted that a maximum pressure development is attained in about 9 days with crude Process B mustard gas. With the ammonia-treated mustard gas a negative pressure actually obtained for 3 days, after which a slight positive pressure was built up. The negative pressure is very likely the result of the neutralization of the ammonia in solution and as a gas by the hydrochloric acid formed by hydrolysis. It is possible that if the tests had extended over a longer period, a pressure as high as with the crude mustard gas would have been obtained. The pressure developed by the ammonia-treated mustard gas in glass is practically nil, and the acidity developed is very slight.

The gas oil-mustard gas mixture in general shows a behavior similar to that of the ammonia-treated materials for the earlier part of the test. However, the pressure soon develops more rapidly and would undoubtedly reach a maximum sooner.

All samples of mustard gas in steel uniformly turned deep black, while the samples in glass remained orange-yellow. (A sample of crude Process B mustard gas, which was a light orange-yellow originally and which was sealed up in a glass tube, turned a deep black after about 16 mo. A sample of pure, colorless mustard gas, however, was still perfectly clear even after 20 mo.)

CONCLUSIONS

1—A decomposition of both Process A (original 60° C. process) and Process B (Levinstein) mustard gas takes place in steel shell at 60° C. The extent of the decomposition is not serious even under the severe conditions of the investigation.

2—Sulfur is deposited in solid form in shell in amounts ranging from 5 to 8 per cent of the liquid content of the shell.

3—The pressure developed in the ordinary steel shell is at most barely two atmospheres in any one shell. This seems to be a maximum or equilibrium pressure, reached after about 9 days.

4—The acid content increases considerably, but the concentration is not sufficiently high to cause serious corrosion.

5—A preliminary treatment of the mustard gas with ammonia gas serves to delay the formation of pressure. This delay is of sufficient length to warrant the preliminary treatment of mustard gas which is to be stored for some length of time in steel shell or containers.

ACKNOWLEDGMENT

The authors desire to thank Major Wm. Lloyd Evans of the Chemical Laboratory, Edgewood Arsenal, for the timely suggestions he has given.

THE PRECIPITATION OF SULFUR FROM CRUDE MUSTARD GAS BY MEANS OF AMMONIA[1]

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Received August 19, 1920

Mustard gas (β,β'-dichloroethyl sulfide) was produced at Edgewood Arsenal by two processes based upon the interaction of liquid sulfur monochloride and ethylene gas. The following equation represents, in brief, the most probable reaction:

$$2C_2H_4 + S_2Cl_2 = (ClC_2H_4)_2S + S$$

The equation, as written, does not indicate the formation of the intermediate compound $ClC_2H_4.S.Cl$ or of the disulfide $S(C_2H_4)_2S$, both of which have been proved to be present in crude mustard gas. An inspection of the equation, however, indicates that one atomic

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weight of free sulfur is formed for every molecular weight of mustard gas produced. Of the total weight of the mustard gas-sulfur mixture, the sulfur constitutes 16.76 per cent.

This sulfur does not precipitate out quantitatively during the course of the reaction. During one process of manufacture (Process A, the 60° C. process) varying percentages (2 to 8) precipitated out in the form of a slimy, amorphous sludge—the greater the moisture content of the ethylene used, the greater the sulfur precipitation. During the other process (Process B, the 30° to 35° C. Levinstein process) none of the sulfur precipitated out when the ethylene gas was reasonably dry. The mustard gas produced by Process A had a marked tendency to precipitate out sulfur on standing, the amount remaining in the mustard gas being about 6 to 8 per cent by weight of the original crude, *i. e.*, about 50 to 60 per cent of the sulfur finally precipitated out, the other remaining in the mustard gas indefinitely. Lowering of the temperature (complete solidification) had the same effect, as far as quantity of sulfur precipitated was concerned. However, in the Process B mustard gas, the sulfur had but an extremely small tendency to separate out as free sulfur; in fact, most of the material produced with dry ethylene showed only a slight sulfur precipitation after a period of a month (a sample kept for 22 mo. in a sealed glass container showed only about a 1 per cent precipitation). Freezing of the sample also did not cause sulfur precipitation; repeated freezing and remelting of a sample of the crude Levinstein mustard gas had no effect on the sulfur "hold-up."

During the course of some experiments with Process A mustard gas to remove the hydrochloric acid produced by the hydrolysis of sulfur monochloride and of mustard gas, Venable and Felsing[1] bubbled moist ammonia gas through crude mustard gas. Immediately crystalline sulfur was deposited in amounts ranging from 5 to 10 per cent of the weight of the mustard gas-sulfur mixture. *Dry* ammonia passed through *dry* mustard gas had no such effect. The melting point of the ammonia-treated mustard gas was never higher, practically always the same, and occasionally slightly lower than before treatment. With the object of ascertaining the effect of ammonia gas upon the crude Process B mustard gas, in which the sulfur hold-up was complete, the following samples were subjected to a uniform ammonia treatment. Moist ammonia gas was passed through the mustard-gas sample for 5 min. The sulfur immediately began to crystallize out. After cooling, the liquid and crystals were allowed to stand in contact for 6 hrs., and the mustard gas was then filtered through a tared Gooch filter. The precipitate, consisting of sulfur and a very small quantity of ferric hydroxide, was washed free of adhering mustard gas with CCl_4 (saturated with sulfur at room temperature). The Gooch was dried at 100° C. and weighed. The ferric hydroxide was then removed with dilute sulfuric acid, and the Gooch reweighed after drying. The following table presents the data obtained:

SAMPLE	Melting Point before Treatment ° C.	Melting Point after Treatment ° C.	Pure Mustard-Gas Content Per cent	Per cent Sulfur Precipitated	Per cent Efficiency of Precipitation
1	9.2	9.20	68.2	6.79	40.50
2	8.7	8.65	71.6	6.54	39.00
3	7.8	7.80	71.5	7.44	44.35
4	7.0	6.90	69.4	7.00	41.72
5	7.4	7.40	64.5	7.10	42.35
6	8.0	8.05	70.0	6.45	37.46
7	8.2	8.10	71.7	7.80	46.50
8	7.2	7.20	71.0	7.20	42.93

In each of the samples described above, *no* sulfur had precipitated out before treatment. The mean weight per cent of sulfur precipitated out was 7.04, which means that only 42 per cent of the supposedly free sulfur was precipitated by the ammonia treatment. The melting points of the samples after treatment were practically the same as before treatment. The pure mustard-gas content was determined on the crude material before treatment by vacuum distillations and melting-point determinations on the distilled product.

From the foregoing observed facts and tabulated data, it is evident that part of the sulfur, at least, is present in the mustard gas as colloidal sulfur, since its removal does not materially influence the melting point of the mustard gas, *i. e.*, does not cause a raising of the melting point, which it would have done if the sulfur had been in true solution. Of course, there is the possibility that the sulfur existed in the mustard gas as a compound, but it is hardly probable that this compound would have the same melting point as the mustard gas. It is also quite apparent that part of the sulfur is present in the form of compounds, since by no agency whatsoever has it been possible to separate all the 16.76 per cent sulfur as such from the body of liquid, without resorting to a vacuum distillation. The sulfur, then, which is in colloidal form in crude Process B mustard gas, is about 40 to 45 per cent, while 55 to 60 per cent are present in the form of compounds.

SUMMARY

1—When mustard gas is produced from sulfur monochloride and ethylene, only part of the free sulfur formed separates out.

2—In some cases moisture, freezing, and long standing cause a partial separation of the sulfur.

3—The addition of moist ammonia causes a precipitation of about 40 to 45 per cent of the total supposedly "free" sulfur.

4—It is pointed out that the observed facts seem to indicate that part of the sulfur is present in the colloidal state, while the other part (55 to 60 per cent) seems to be present in the form of compounds.

ACKNOWLEDGMENT

The authors desire to thank Major Wm. Lloyd Evans of the Chemical Laboratory, Edgewood Arsenal, for the timely suggestions he has given.

THE INTERSOLUBILITY OF CHLOROPICRIN AND WATER[1]

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SOLUBILITY OF CHLOROPICRIN IN WATER

Chloropicrin was shaken with a large amount of distilled water to form an emulsion. The mixture was

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[1] Cleveland Laboratory, Edgewood Arsenal Report, June 18, 1918.

[1] Published by permission of the Chief of the Chemical Warfare Service.

permitted to stand for 3 days at room temperature in order to allow the chloropicrin to settle. The water solution was then maintained at 25° C. for 6 hrs., and 100 cc. samples were analyzed by the method described below.

The solubility of chloropicrin in water at 0° was determined by shaking thoroughly and standing for several days in a thermostat at 0°. Samples of the clear solution were treated by the method given below. If portions of this solution were brought to room temperature, a decided precipitation of chloropicrin resulted. Upon cooling, the emulsion would disappear and the solution again become clear.

The solubility at 75° C. was obtained by putting the 0° solution for 2 days in a thermostat maintained at 75° to 76°. The flask holding the solution was stoppered in order to prevent evaporation.

METHOD OF ANALYSIS FOR CHLOROPICRIN IN WATER[1]—Fifty cc. of alcoholic sodium sulfite were added to each sample. (This solution was prepared by dissolving 10 g. of hydrated sodium sulfite in 250 cc. of water and diluting with an equal volume of ethyl alcohol.) The sample was refluxed with an air condenser to eliminate alcohol, the refluxing being continued until all but 10 cc. of the solution had evaporated. It was then diluted to 100 cc., and a standard solution of silver nitrate added in excess, together with 10 cc. of nitric acid. After boiling to expel the nitrous fumes and to coagulate the silver chloride, the solution was cooled and the excess silver nitrate titrated with a standard solution of ammonium thiocyanate, using ferric alum as an indicator.

TABLE I

	Temperature ° C		
	0	25	75
Grams chlorine in 100 cc. H_2O	0.1472	0.1060	0.0739
	0.1465	0.1048	0.0753
	0.1468	0.1049	0.0695
	...	0.1049	0.0674
	...	0.1042	0.0796
	...	0.1055	0.0768
	...	0.1045	0.0674
Average equivalent chloropicrin	0.2272	0.1621	0.1141

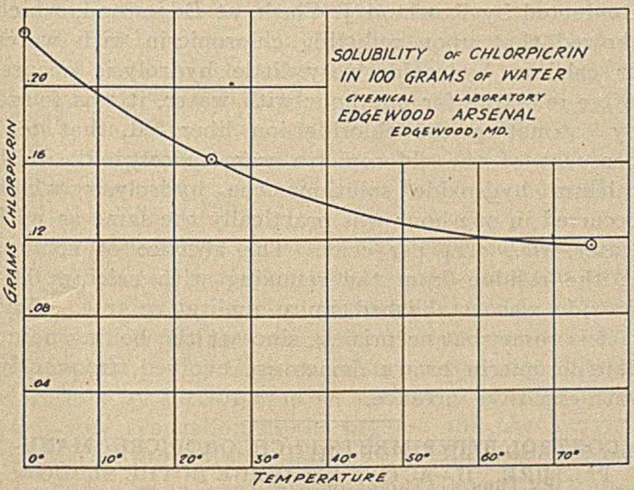

FIG. 1

Table I gives the results obtained by the analysis of the chloropicrin dissolved in water at various temperatures. The data are illustrated by the curve in Fig. 1.

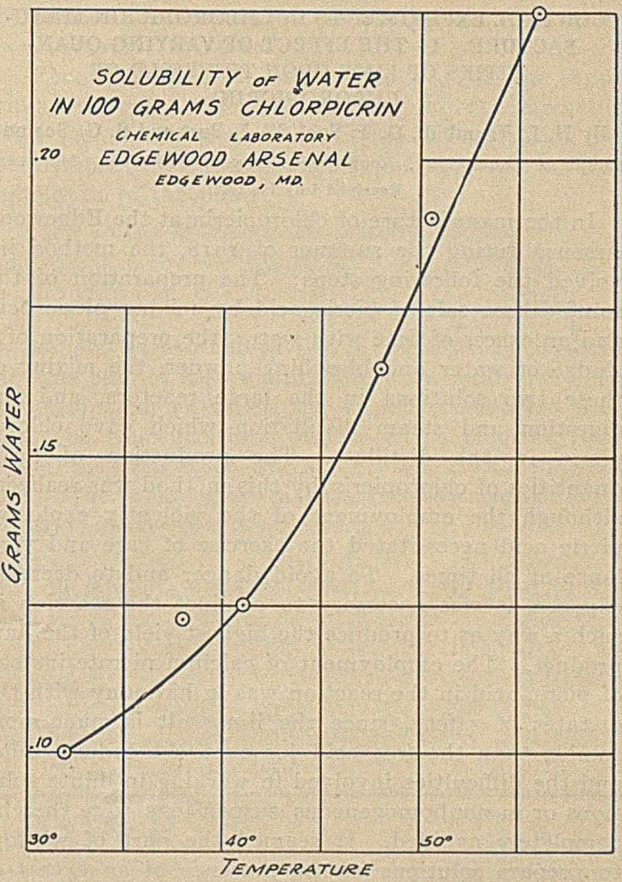

FIG. 2

SOLUBILITY OF WATER IN CHLOROPICRIN

The apparatus consisted of a glass cylinder, sealed at one end and fitted at the other with a two-hole rubber stopper. A thermometer was placed in one hole of the stopper and a small glass tube, the length of the stopper, in the other. Through this tube was introduced a glass stirring rod with a loop at one end. Chloropicrin was placed in the apparatus and very small portions of water introduced. The mixture was slowly heated and constantly stirred until all the water had gone into solution. The apparatus was then cooled and the temperature noted at which a white cloud appeared in the solution, due to the precipitation of water. The tube was again heated and the temperature at which the solution cleared was noted. The average of the temperatures for precipitation and the clearing of the solution was taken as the temperature of solubility. The data collected are reported in Table II and illustrated in the accompanying solubility curve (Fig. 2).

TABLE II

H_2O Gram	Chloropicrin		Temperature of Miscibility ° C.	H_2O per 100 G. Chloropicrin
	Cc.	G.		
0.1098	29.3	48.49	55	0.2265
0.1098	35.8	59.25	50.8	0.1853
0.1098	40.3	66.70	48	0.1647
0.1098	53.4	88.38	41	0.1243
0.1098	56.0	92.68	36	0.1185
0.1098	66.0	109.25	32	0.1003

CONCLUSIONS

1—Chloropicrin is only slightly soluble in water, the solubility decreasing with increase in temperature.

2—Water is only slightly soluble in chloropicrin, the solubility increasing with increase in temperature.

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[1] This method was secured from the Bureau of Mines.

CONTROL EXPERIMENTS IN CHLOROPICRIN MANUFACTURE. I—THE EFFECT OF VARYING QUANTITIES OF LIME UPON THE YIELD OF CHLOROPICRIN[1]

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Received July 14, 1920

In the manufacture of chloropicrin at the Edgewood Arsenal during the summer of 1918, the method involved the following steps: The preparation of the soluble lime salt of picric acid by mixing picric acid and an excess of lime with water, the preparation of a sludge of water and bleaching powder, the mixing of these two solutions in the large reactors, and the digestion and steam distillation which gave chloropicrin in the distillate. The production of large quantities of chloropicrin by this method was realized, although the employment of the violently explosive picric acid necessitated the exercise of care and vigilance at all times. To avoid danger and to decrease expense, it was necessary to conduct the reaction in such a way as to produce the highest yield of the final product. The employment of calcium picrate instead of picric acid in the reaction was in harmony with the dictates of safety, since the lime salt is much more soluble than the free acid (or even the sodium salt), and the difficulties involved in working in dilute solutions or in nonhomogeneous suspensions were thereby completely avoided. It seemed the part of wisdom to prepare solutions in the presence of an excess of lime which served as a margin of safety in the operation of the process. The laboratory was requested to investigate the effect of adding varying quantities of lime upon the yields of chloropicrin.

EXPERIMENTAL METHOD

The materials employed for the preparation of chloropicrin were carefully analyzed, with the following results:

Lime	95.54 per cent CaO
Picric acid	99.80 per cent free acid, no sulfates
Bleaching powder	
Sample 1	33.30 per cent available chlorine
Sample 2	32.21 per cent available chlorine
Sample 3	33.3 per cent available chlorine

The best yields were obtained when the bleaching powder was made up to a thick paste with water, and the solution of picric acid or calcium picrate, as the case might be, was added in small portions with shaking and cooling, the temperature being kept below 30° C. The loss of chloropicrin was prevented by keeping the flask tightly stoppered during the addition. For a neutral solution 300 g. of bleaching powder, 30 g. of picric acid, and 3.85 g. of lime were employed.

Before conducting the steam distillation, the flask was connected to the condenser and gently heated until the yellow color had disappeared. Too rapid heating at this point not only led to lower yields of chloropicrin but also left a yellow residue, which was not decolorized upon subsequent treatment with bleaching powder, followed by steam distillation. From the distillate the chloropicrin lower layer was drawn off and weighed, the amount dissolved in the aqueous layer being estimated from the solubility curve. Ordinarily, the latter quantity increased the yield by about 1 per cent. Yields are reported on the basis of the ratio by weight of chloropicrin to picric acid.

To illustrate the importance of keeping the mixture cool during the picric acid or picrate addition, four experiments were conducted in which the picric acid was added in one step without cooling, the ratios obtained being 1.68, 1.68, 1.67, and 1.65. Upon repetition of the experiment with cooling and stepwise addition of the picric acid, the ratio was 1.75 in two experiments.

In all the experiments, 30 g. picric acid, 300 g. bleaching powder, and 1200 g. water were employed.

The yields obtained by varying the amount of lime are shown in the following table:

Amount of Lime	$\frac{\text{Wt. of Chloropicrin}}{\text{Wt. of Picric Acid}}$
0	1.76
	1.75
	1.75
3.85 g. (no excess)	1.76
	1.80
	1.73
	1.79
	1.75
	1.74
	1.78
4.24 g. (10 per cent excess)	1.72
	1.76
	1.78
	1.78
	1.79
	1.69
	1.71
	1.76
	1.77
	1.76
5.00 g. (30 per cent excess)	1.72
	1.69
	1.67
	1.78
	1.79
	1.82
	1.79
	1.78
	1.78

CONCLUSION

Under conditions which approximated as closely as possible those employed in the chloropicrin plant at Edgewood Arsenal, an excess of lime had no influence upon the yield of chloropicrin. Indirect support of this conclusion was furnished by some experiments conducted by Rowland J. Clark, at Edgewood, which showed that upon refluxing chloropicrin with water or calcium hydroxide very little hydrolysis occurs. After refluxing for one hour with water, it was found by estimating the chloride ion liberated, that 0.21 per cent of the chloropicrin was hydrolyzed. With calcium hydroxide solutions the hydrolysis which occurred in one hour was practically the same as with water, *viz.*, 0.24 per cent. The absence of nitrites in the residue from the refluxing with calcium hydroxide was established by a qualitative test. This fact is somewhat surprising, since at the boiling point of chloropicrin brown fumes are evolved, frequently with explosive violence.

CONTROL EXPERIMENTS IN CHLOROPICRIN MANUFACTURE. II—ACTIVE CHLORINE IN THE SLUDGE FROM THE MANUFACTURE OF CHLOROPICRIN[1]

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In the manufacture of chloropicrin it was necessary to use a fairly large excess of bleaching powder in

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order to decompose completely the calcium picrate during the steam distillation. It was obviously desirable to know what happened to this excess of bleaching powder during the steam distillation.

The following experiments establish the approximate rate at which active chlorine disappears during steam distillation, first, in the residue left after the preparation of chloropicrin, and, second, in a more concentrated solution containing the same concentration of bleaching powder as that originally present in the chloropicrin stills. Finally, analyses were made to determine the concentration of active chlorine remaining in each of the ten plant stills at the end of the distillation which removed the chloropicrin from the sludge.

Table I—Percentages of Active Chlorine

After Distilling off Chloropicrin	After 0.5 Hr. Steam Distillation	After 1.5 Hrs. Steam Distillation
0.0330	0.0262	0.0157
0.0505	0.0218	0.0172
0.0459	0.0242	0.0160

The residue left in the flask when chloropicrin was prepared as described in the preceding paper was analyzed for available chlorine by the iodometric method. The sludge was then subjected to steam distillation for periods of one-half and one and one-half hours, respectively. The analyses furnish approximate data for the rate at which bleaching powder is decomposed by steam.

When higher initial concentrations of the hypochlorite were employed, the rate of decomposition with steam was noticeably higher. The initial concentrations shown in Table II correspond to those employed in the plant.

Table II—Percentages of Active Chlorine

Initial	After 1 Hr. Steam Distillation	After 2 Hrs. Steam Distillation
6.98	2.52	0.714
6.18	3.21	0.747

Samples of the sludge left in the chloropicrin stills at the end of the distillation were analyzed. The conditions under which the various runs were made and the concentrations of the active chlorine based upon the weight of the sludge are shown in Table III. The results show that the concentration of active chlorine is very low in all cases.

Table III

No. of Still	Max. Temp. during Distillation	Percentage Active Cl in Sludge
1	102.0	0.28
2	103.5	0.24
3	104.0	0.28
4	105.0	0.28
5	100.0	0.285
6	104.0	0.32
7	104.0	0.29
8	105.0	0.29
9	101.0	0.26
10	104.0	0.22

ORIGINAL PAPERS

A STUDY OF THE REACTIONS OF COAL SULFUR IN THE COKING PROCESS[1,2]

By Alfred R. Powell

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PREVIOUS INVESTIGATIONS

The sulfur of coal has now been definitely established to exist as pyrite or marcasite, FeS_2, organic sulfur, and a rather small amount of sulfates, and accurate methods have been devised for the determination of these different forms.[3] The behavior of each form during the destructive distillation of coal is of theoretical interest, as well as of the greatest technical importance, since the reactions of the coal sulfur will determine the percentage of sulfur left in the coke and the nature and the amount of the sulfur compounds in the by-products.

The percentage of coal sulfur expelled during the coking process varies over wide limits, and this variation has always been supposed to be due to different relative percentages of sulfur forms in the coal.[4] M'Callum states[5] that he separated coal into different fractions by specific gravity methods, thereby securing a partial separation of the organic and the inorganic sulfur. From coking tests on these fractions he concluded that a somewhat greater percentage of the organic sulfur was volatilized than the inorganic, but no very sharply cut difference was noticeable. J. R. Campbell[1] stated that most of the coal sulfur was present as pyrite, that 42 per cent of this was volatilized during the coking process, and that the remainder was left in the coke as pyrrhotite. He also stated that most of the organic sulfur was retained in the coke.

Some tentative conclusions have been drawn by S. W. Parr[2] concerning sulfur in the coking process from his work on the low temperature carbonization of coal. He states that "the organic sulfur in the raw coal and half of the sulfur of FeS_2 is for the most part discharged at relatively low temperatures." This occurs at about 500° C. At about 700°, the sulfur of the FeS formed from the FeS_2 is taken up by carbon, leaving free iron in the coke.

It therefore appears that different investigators have obtained widely divergent results, and have advanced many different theories as to the reactions undergone by the coal sulfur during carbonization. The present investigation was undertaken with the idea of carbonizing a variety of coals under carefully controlled conditions, and studying the character and amount of the various sulfur compounds formed. Since these analyses were to be made over every period of the carbonization process, a complete and detailed picture could be obtained of the changes occurring in the coal sulfur.

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[1] Published by permission of the Director of the U. S. Bureau of Mines.

[2] Presented by title at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[3] A. R. Powell and S. W. Parr, "A Study of the Forms in Which Sulfur Occurs in Coal," University of Illinois, Engineering Experiment Station, *Bulletin* **111** (1919).

[4] Fulton, "Treatise on Coke," International Textbook Co., Scranton, Pa., **1905**, pp. 38–40.

[5] *Chem. Eng.*, **11** (1910), 27.

[1] *Bull. Am. Inst. Mining Eng.*, **1916**, 177.

[2] *Ibid.*, **1919**, 1807.

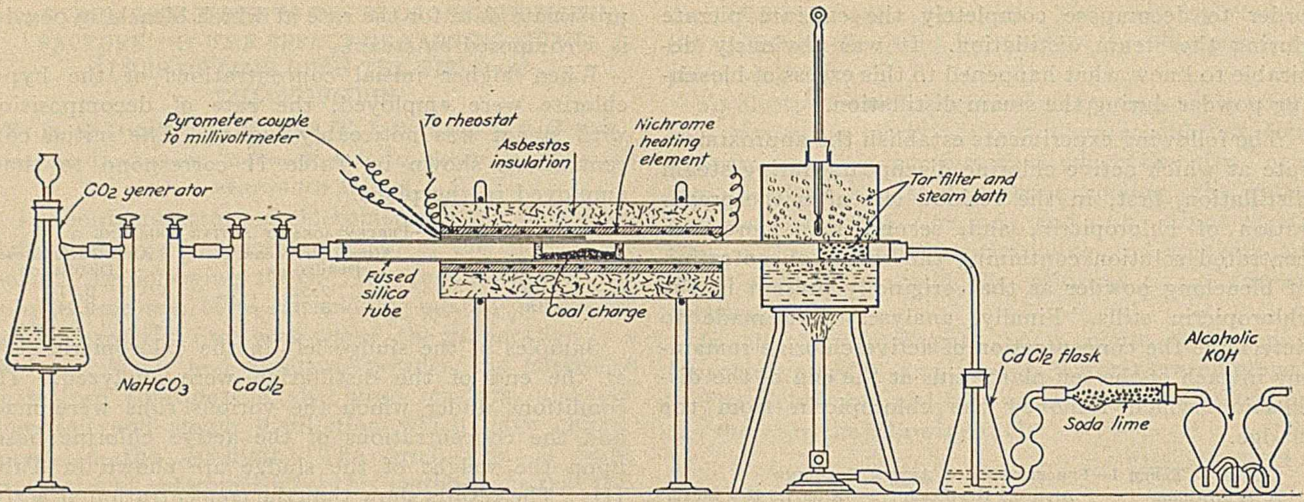

FIG. 1—APPARATUS USED IN THE STUDY OF COAL SULFUR CONVERSION IN THE COKING PROCESS

APPARATUS

The apparatus was designed to coke about 5 g. of coal, and was so arranged that the temperature of the coking chamber could be controlled at all times to within a few degrees. At first thought, criticism might be made of this procedure, in that the quantity of coal used was so small. However, when it is considered that the primary coking reaction was desired, without the secondary effects produced by the travel of the gases through the hot coking mass, it is seen that the use of such a small quantity is essential. Furthermore, uniform temperature and close temperature control are impossible with a large quantity of coal.

Details of the coking apparatus as finally perfected are shown in Fig. 1. The coking chamber consisted of a five-eighths inch fused silica tube. The coking charge of 5 g. of the powdered coal was evenly distributed over 4 in. of the middle portion, with asbestos plugs at each end of the charge. A cotton plug was placed at the outlet end of the tube to act as a tar filter.

The charge was heated by a nichrome-wound tube furnace, which consisted of an alundum tube, of a somewhat greater diameter than the tube containing the charge, around which was wound nichrome wire of such a size and length that 1000° could be easily attained. The resistance wire was set in a mixture of alundum cement and water glass, and heat insulation was obtained by wrapping around the furnace several layers of heavy asbestos paper. Temperature readings were taken by means of a Hoskins thermocouple, the end of which rested against the outside of the coking tube at the point where the coal charge had been placed. Since the temperature of the run was maintained for 2 hrs. in the furnace, the temperature on the outside and inside of the silica tube must have been the same.

A slow stream of dry carbon dioxide was passed into the inlet end of the coking tube during certain periods of the run to act as a rinsing agent. This carbon dioxide was generated by the action of hydrochloric acid on calcium carbonate, and was passed through sodium bicarbonate and calcium chloride. This procedure was followed only at the beginning of a run to insure a non-oxidizing atmosphere over the coking charge, and at the end of the run to rinse out the last traces of volatile sulfur compounds.

The outlet and tar filter end of the tube was surrounded by a copper water bath of the design used by the Steel Corporation for the same purpose. By means of this device the temperature of the tar filter was at all times kept at 90°. The gas from the outlet end of the tube passed directly into a flask containing ammoniacal cadmium chloride which removed the hydrogen sulfide. The gas then passed through an absorption bulb containing absolute alcoholic potash, by means of which the presence of carbon bisulfide could be established. This last absorption bulb was replaced in certain runs by a Referee's total sulfur apparatus.

METHOD OF PROCEDURE

After the charge of coal had been placed in the tube and the steam bath around the tar filter brought up to the required temperature, a stream of carbon dioxide was started through the tube, and at the same time the heating current was turned on. After a few minutes the carbon dioxide was shut off, and the electric current was carefully regulated by means of a rheostat so as to bring the temperature slowly up to that required for the run. In the case of the higher temperature runs this gradual increase sometimes required as much as one hour.

SULFUR IN TAR—The run was continued for 2 hrs. at the temperature desired, this length of time being considered necessary to bring the reactions to equilibrium. The current was then shut off and carbon dioxide again run through for a few minutes. The coking tube was removed from the furnace, and as much of the tar as possible taken out for a sulfur analysis, which was made by the use of Eschka mixture. This determination must be considered only approximate, but, since it involved such a small portion of the coal sulfur, was sufficiently accurate for this investigation.

SULFUR IN COKE—The coke was shoved out of the tube by means of a long iron rod, separated as thoroughly as possible from the asbestos plugs, and ground

TABLE I—SOURCE AND PROXIMATE ANALYSIS OF COALS USED IN EXPERIMENTS

No.	NAME	SOURCE	Moisture	Volatile Matter	Fixed Carbon	Ash	Sulfur
21100	Tennessee	Tennessee, Morgan Co. Coal Creek, Couger-Baker	0.74	39.05	52.40	7.80	4.25
20507	Pocahontas	West Virginia, McDowell Co., Pocahontas No. 3, Mine No. 7	0.39	22.88	70.47	6.25	0.56
18847	Pittsburgh	Pennsylvania, Bruceton, Experimental Mine, Bureau of Mines	1.57	38.72	54.95	4.75	1.72
23066	Upper Freeport	Pennsylvania, Butler Co., Upper Freeport, Cunningham Coal Co.	2.04	33.11	56.36	8.49	1.21
33945	Joliet	Mixture of 65% Pocahontas, 20% Lynch, Ky., and 15% washed Franklin Co., Ill., coal. As charged at coke ovens, Illinois Steel Co., Joliet	0.92	26.28	65.60	7.20	0.82
33819	Raw Vandalia	Vandalia, Ind.	2.35	38.05	49.60	10.00	1.38
33820	Washed Vandalia	Vandalia, Ind. Same as above but washed	2.48	39.52	50.73	7.27	1.18

[1] All samples were in an air-dry condition.

in a porcelain mortar to 100-mesh size. It was then placed in a flask so arranged that a current of hydrogen could be passed through and the outgoing gas bubbled through ammoniacal cadmium chloride. One hundred cc. of a 1:1 mixture of concentrated hydrochloric acid and water were poured over the coke and the contents of the flask heated to boiling, for about 15 min., while a brisk stream of hydrogen was passed through. The hydrogen sulfide given off was a measure of the metallic sulfide content of the coke, that is, the ferrous sulfide and pyrrhotite. It was estimated by treating the cadmium sulfide precipitate with an excess of hydrochloric acid and standard iodine solution, and titrating back with thiosulfate.

A sulfur analysis of the hydrochloric acid extract filtered off from the coke gave the sulfate content of the coke. The coke was then treated with 1:3 mixture of concentrated nitric acid and water, and allowed to stand at room temperature for 24 hrs. The extract was filtered, the nitric acid evaporated off, and sulfur and iron determined in the resulting residue. By this means the undecomposed pyrite of the coke was figured. The iron value proved to be a good means of checking the sulfur, since the iron-sulfur ratio proved whether or not the nitric acid had selectively extracted pyrite.

In most cases the residual coke was discarded, the sulfur in it being calculated by difference, but in a few runs the sulfur was determined directly. In all such cases the sum of the sulfur determinations checked very closely with the total sulfur of the coal.

SULFUR IN VOLATILE MATTER—The sulfur which had been given off from the coal in the form of hydrogen sulfide had been caught in the ammoniacal cadmium chloride flask of the coking apparatus. It was estimated as just described under the determination of metallic sulfide in the coke. Carbon bisulfide in the volatile matter was tested for by boiling the contents of the alcoholic potash absorption bulb, acidifying with acetic acid, and adding copper acetate. The presence of a reddish brown precipitate would indicate carbon bisulfide.

DESCRIPTION OF COALS USED

Eight coals were used during these investigations. Table I gives the laboratory number, the name under which the coal will be referred to hereafter, a general description of the source, and the proximate analysis of each coal.

TABLE II—ANALYSIS OF SULFUR FORMS
(Values given in per cent, air-dry basis)

No.	COAL	Total	Pyritic	Sulfate	Organic
21100	Tennessee	4.25	1.75	0.71	1.79
20507	Pocahontas	0.56	0.08	0.01	0.47
18847	Pittsburgh	1.72	0.79	0.23	0.70
23066	Upper Freeport	1.21	0.47	0.07	0.67
33945	Joliet	0.82	0.26	0.00	0.56
33819	Raw Vandalia	1.38	0.70	0.03	0.65
33820	Washed Vandalia	1.18	0.25	0.03	0.90

A complete analysis, by the method of Powell and Parr,[1] was made on all the coals for the different forms of sulfur present. The results are given in Table II.

EXPERIMENTAL RESULTS

EFFECT OF TEMPERATURE ON PYRITE—Since pyrite is one of the most important sulfur constituents of coal, it was necessary to study its behavior at different temperatures before going ahead with the study of coal itself. Very little pyrite was decomposed up to 500°, but at 1000° the decomposition was complete. Table III shows the changes in the forms of sulfur in mineralogical pyrite between 0° and 1000°.

TABLE III—ANALYSIS OF PYRITE BEFORE AND AFTER DECOMPOSITION AT 1000° C.

	0° C.	1000° C.
Pyritic Sulfur	48.52	0.00
Sulfate Sulfur	0.16	0.00
Free Sulfur	0.00	21.88
Sulfide Sulfur	0.00	24.24
Sulfur as H_2S	0.00	2.56
TOTAL	48.68	48.68

These results point pretty clearly to the following reaction:

$$FeS_2 = FeS + S$$

The sulfide content of the decomposed pyrite is practically in quantitative accordance with this reaction. Owing to the presence of moisture or other hydrogen yielding bodies, a small part of the free sulfur has been converted into hydrogen sulfide.

After pyrite has been heated the residue is almost invariably magnetic. This is not due to the presence of free iron but to the fact that the residue is not plain ferrous sulfide, but pyrrhotite, or magnetic sulfide of iron. It has been shown that pyrrhotite is not a definite compound, but is a solid solution of sulfur in ferrous sulfide.[2] The amount of sulfur which is present in the sulfide is determined by the temperature and the partial pressure of free sulfur over it. In an atmosphere of hydrogen sulfide, the maximum amount of sulfur retained in ferrous sulfide is 6.0 per cent at 600°. At 1000° the percentage is 3.5 per cent, and at 1300° it is 2.0 per cent.

At 1000° the partial pressure of free sulfur in an atmosphere of hydrogen sulfide is 70 mm., or a little less than one-tenth of an atmosphere. This amount of free sulfur in the space above the pyrrhotite holds its content of dissolved sulfur at 3.5 per cent, as has been stated. If, however, as is true in actual practice, the amount of hydrogen sulfide, and therefore the amount of free sulfur, present is very small, the percentage of sulfur dissolved in the ferrous sulfide is very much less than 3.5 per cent. When the residue from the heated pyrite was dissolved in acid, the sulfur left undissolved and in the free state was denoted by a very slight cloudiness of the solution. The

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[1] *Loc. cit.*

[2] E. T. Allen, J. L. Crenshaw and John Johnston, "The Mineral Sulfides of Iron," *Am. J. Sci.*, **33** (1912), 169.

indications were that it would amount to only a very small fraction of one per cent. Under these circumstances, it can be neglected for quantitative purposes, although it explains the weakly magnetic character of the pyrite residue.

Because of these considerations, all the calculations of this investigation have been based on the decomposition of pyrite to form ferrous sulfide and free sulfur, but it must be remembered that a small part of the sulfur remains in the ferrous sulfide in the form of a solid solution.

No free iron existed in the residue from decomposed pyrite or in finished coke, as shown by microscopic tests. When an acid solution of a copper salt was added to the finely powdered substance no metallic copper could be detected under the microscope, thus proving the absence of free iron.

DECOMPOSITION OF PYRITE-COAL MIXTURE—A further study of the decomposition products of pyrite was made, in which the pyrite was incorporated with a coal of known composition, so that all secondary reactions could be noted. The mixture contained 50 per cent of mineralogical pyrite and 50 per cent of Tennessee coal. The results of this test are given in Table IV.

TABLE IV—DECOMPOSITION OF PYRITE-COAL MIXTURE AT 1000° C.

	0°	1000°
Pyritic Sulfur	25.14	0.00
Sulfate Sulfur	0.39	0.00
Organic Sulfur	0.90	1.93
Free Sulfur	0.00	5.22
Sulfide Sulfur	0.00	13.12
Sulfur as H_2S	0.00	6.08
Tar Sulfur	0.00	0.08
TOTAL	26.43	26.43

It may safely be assumed that the sulfate form will be reduced to the sulfide. Subtracting the sulfide sulfur from this source from the total sulfide sulfur leaves 12.73 per cent as the sulfide sulfur coming from the pyrite. This figure is very close to 12.57 per cent or one-half the pyrite sulfur. The complete decomposition of pyrite in coal must therefore yield ferrous sulfide and free sulfur, which later changes to hydrogen sulfide if an excess of hydrogen yielding matter is present.

TENNESSEE COAL—The results of a complete study made upon the Tennessee coal of sulfur distribution at different temperatures are given in Table V.

It will be noted that the sulfur not found in any other type of compound is placed under the head of "organic sulfur." That the coal sulfur other than that of the pyrite and sulfates is organic in nature has been proved.[1] This organic sulfur persists almost unchanged in type up to 400°. Between 400° and 500° a decided change in its characteristics takes place. This is shown by the fact that treatment with nitric acid and subsequent treatment with ammonia does not take into solution the compounds containing the organic sulfur.

That organic sulfur is present, even in the finished coke, and that its percentage is higher in the coke than it was in the original coal has been well proved by Wibaut and Stoffel,[2] who have produced a form of organic sulfur much resembling that of the coke by heating together sulfur and sugar.

From the results given in Table V, it is possible to calculate the nature and magnitude of the probable reactions undergone by the various forms of coal sulfur during the coking process. This is simplified by the preliminary study of pyrite decomposition. In the presence of a large excess of coal substance, pyrite decomposes quantitatively into ferrous sulfide and hydrogen sulfide. Also it may safely be assumed that any sulfate present will be reduced to sulfide. The pyrite decomposed will give a measure of the hydrogen sulfide from this source, but in every case the actual hydrogen sulfide produced is greater than this. A probable source of this excess hydrogen sulfide is the organic sulfur, which makes a third probable reaction. The sulfur of the tar, being entirely of an organic nature, must find its origin in the organic sulfur of the coal. This makes a fourth measurable reaction. It may be noticed that the sulfide sulfur of the coke is generally present in smaller amount than would be formed from the decomposition of the pyrite and the reduction of the sulfate form. This seems to be accounted for by a rather peculiar reaction, namely, the transference of a portion of the sulfur combined as sulfide to a sulfur-carbon combination. This fifth reaction has been noted by other investigators.[1] The evidence for this last reaction is simply the fact that during the latter stages of the coking process there is quite a decided increase in the sulfur held in the carbon-sulfur combination, with a decrease in the amount of sulfides present. The carbon-sulfur combination formed by this reaction has all the properties of the remainder of the sulfur existing in this form in the coke.

TABLE V—DISTRIBUTION OF SULFUR IN TENNESSEE COAL No. 21100
(Values given in percentage by weight of original air-dried coal)

	0°	300°	400°	500°	600°	1000°
Pyritic Sulfur	1.75	1.75	1.42	0.31	0.00	0.00
Sulfate Sulfur	0.71	0.55	0.44	0.01	0.01	0.00
Organic Sulfur	1.79	1.63	1.51	1.70	1.87	1.81
Sulfide Sulfur	0.00	0.13	0.44	0.93	0.82	0.84
Sulfur as H_2S	0.00	0.19	0.39	1.20	1.39	1.44
Tar Sulfur	0.00	0.00	0.05	0.10	0.16	0.16
Sulfur as CS_2	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	4.25	4.25	4.25	4.25	4.25	4.25

TABLE VI—REACTIONS OCCURRING IN CARBONIZATION OF TENNESSEE COAL (Results expressed in per cent sulfur on basis of air-dried coal)

Temperature Range ° C.	FeS_2 = FeS + H_2S	MSO_4 = MS	Organic S = H_2S	Organic S = Tar S	MS = Organic S
0–300	0.00	0.16	0.19	0.00	0.00
300–400	0.33	0.11	0.05	0.05	0.00
400–500	1.11	0.43	0.25	0.05	0.49
500–600	0.31	0.00	0.03	0.06	0.26
600–1000	0.00	0.01	0.05	0.00	—0.02
TOTAL	1.75	0.71	0.57	0.16	0.73

In addition to the five reactions or classes of reactions enumerated above, there are several others which have been noted but have not been measured, owing either to their complexity or to difficulties of analysis. Prominent among these is the formation of pyrrhotite, already noted, and the decided transformation in the characteristics of the organic sulfur compounds between 400° and 500°. Other reactions, of a secondary nature, also occur in retorts. Reactions between the organic sulfur compounds and hydrogen of the gas to form hydrogen sulfide, and between

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[1] Powell and Parr, *Loc. cit.*

[2] *Rec. trav. chim.*, **38** (1919), 132.

[1] S. W. Parr, *Am. Inst. Mining Eng.*, **1919**, 1807; J. P. Wibaut and A. Stoffel, *Loc. cit.*

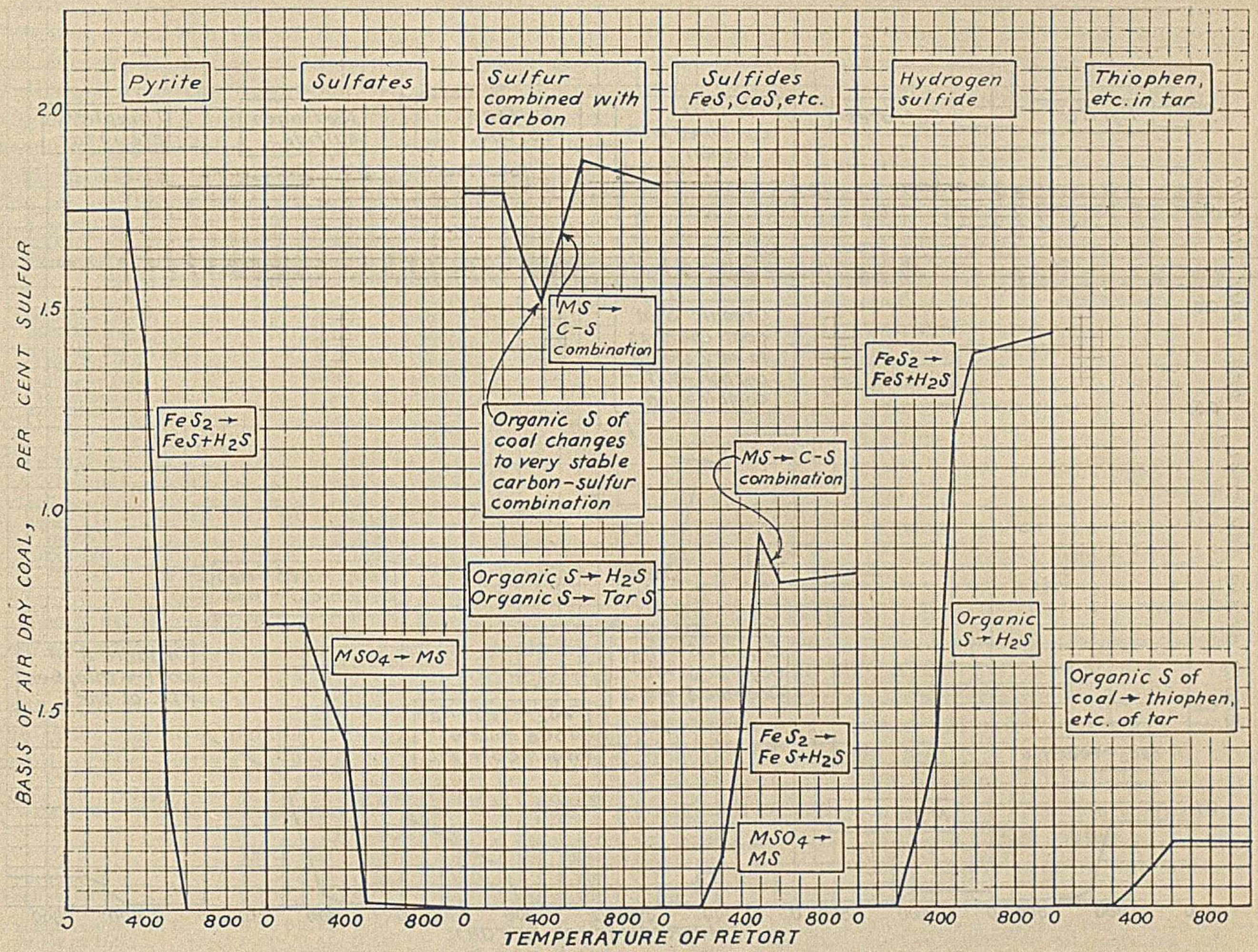

Fig. 2—Series of Curves Showing Variations of Sulfur Constituents at Successive Temperatures of Distillation of Tennessee Coal, No. 21100. Reactions Causing the Variations Are Noted

hydrogen sulfide and red-hot coke to form carbon bisulfide may be mentioned as typical. That carbon bisulfide is not a primary product of coal distillation is shown by the results obtained above. This fact has been known for some time.[1]

Following the facts given above, the magnitude of each of the five measurable reactions has been calculated for each temperature range. A summary of these calculations is given in Table VI, the results being expressed in the per cent of sulfur undergoing the reaction on the basis of the original air-dried coal. It was necessary to express results in this manner in order to get comparable figures.

The courses of these reactions are represented graphically in Fig. 2. The decomposition of the pyrite begins at 300°, is complete at 600°, and reaches its maximum between 400° and 500°. The reduction of the sulfates is practically complete at 500°. From one-quarter to one-third of the organic sulfur is decomposed with the production of H_2S, this decomposition occurring for the most part below 500°. At the lower temperatures of coking, a small part of the organic sulfur finds its way into the tar. Not more than one-tenth of the coal organic sulfur is so distributed. From 400° to 500° a large part of the ferrous sulfide is decomposed, the sulfur apparently entering into combination with the carbon.

POCAHONTAS COAL—The values for sulfur distribution in the Pocahontas coal are given in Table VII, and a summary of its reactions in Table VIII.

Table VII—Distribution of Sulfur in Pocahontas Coal, No. 20507
(Values given in per cent of original air-dried coal)

	0°	300°	400°	500°	600°	1000°
Pyritic Sulfur..........	0.08	0.07	0.09	0.01	0.00	0.00
Sulfate Sulfur..........	0.01	0.02	0.02	0.00	0.00	0.00
Organic Sulfur.........	0.47	0.47	0.44	0.43	0.35	0.27
Sulfide Sulfur..........	0.00	0.00	0.00	0.04	0.05	0.09
Sulfur as H_2S..........	0.00	0.00	0.01	0.06	0.13	0.17
Tar Sulfur.............	0.00	0.00	0.00	0.02	0.03	0.03
Sulfur as CS_2...........	0.00	0.00	0.00	0.00	0.00	0.00
Total..............	0.56	0.56	0.56	0.56	0.56	0.56

Table VIII—Reactions Occurring in Carbonization of Pocahontas Coal (Results expressed in per cent sulfur on basis of air-dry coal)

Temperature Range, ° C.	$FeS_2 = FeS + H_2S$	$MSO_4 = MS$	Organic S $= H_2S$	Organic S = Tar S	MS = Organic S
0–300	0.00	0.00	0.00	0.00	0.00
300–400	0.00	0.00	0.01	0.00	0.00
400–500	0.07	0.01	0.01	0.02	0.00
500–600	0.01	0.00	0.07	0.01	—0.01
600–1000	0.00	0.00	0.04	0.00	—0.04
Total	0.08	0.01	0.13	0.03	—0.05

This coal differs from the Tennessee coal in that it is of a semi-bituminous type and also in the fact that its sulfur content is considerably lower. Furthermore, a very large proportion of the total sulfur is organic, with very little pyrite and practically no sulfate. This may account for some of the differences in the reactions between the two coals.

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[1] Lewes, "The Carbonization of Coal," John Allan & Co., **1912**, p. 274.

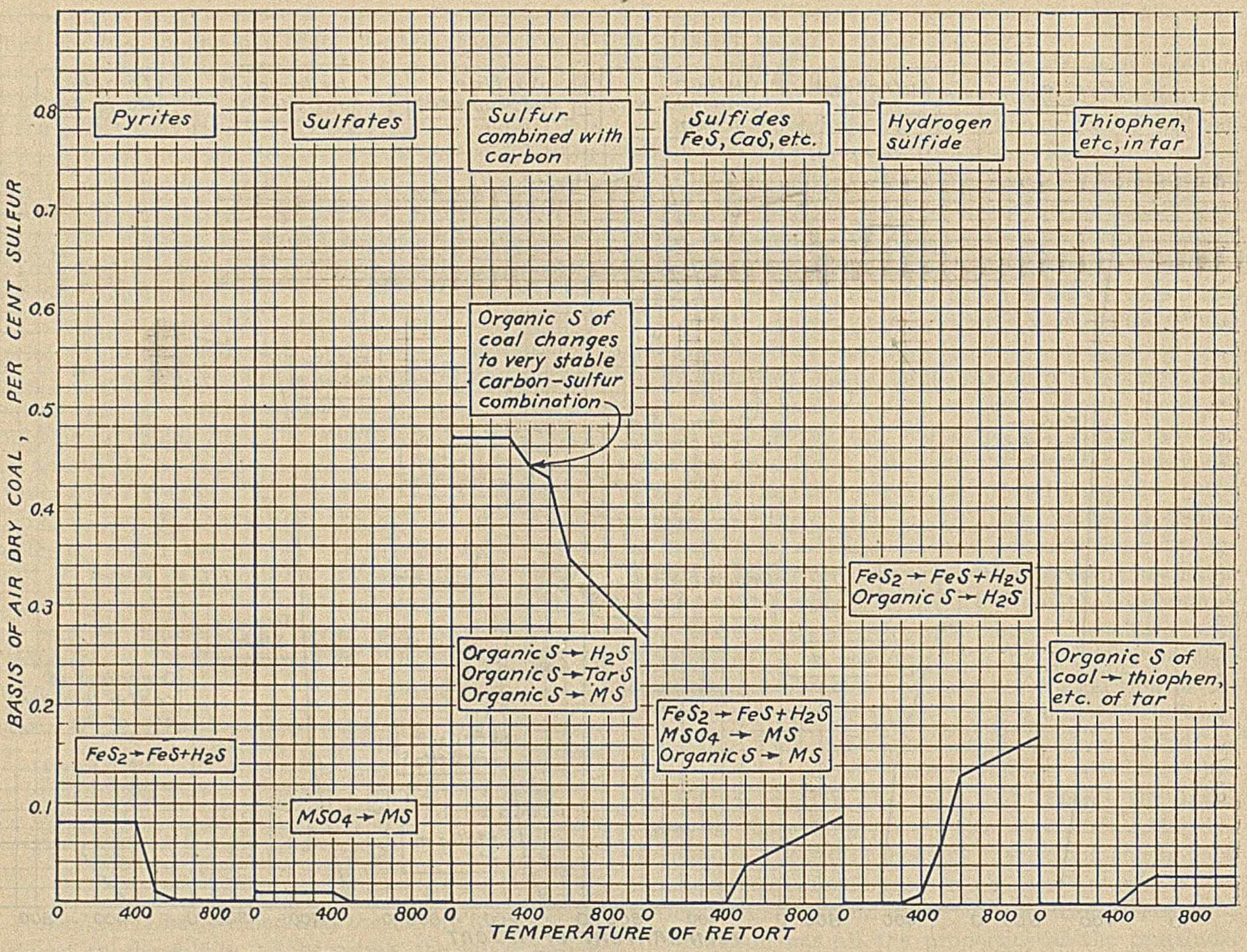

FIG. 3—SERIES OF CURVES SHOWING VARIATIONS OF SULFUR CONSTITUENTS AT SUCCESSIVE TEMPERATURES OF DISTILLATION OF POCAHONTAS COAL, No. 20507. REACTIONS CAUSING THE VARIATIONS ARE NOTED

The reactions of the sulfur in the Pocahontas coal are shown graphically in Fig. 3. In two particulars, these reactions differ materially from those of the Tennessee coal. The decomposition of the organic sulfur to form hydrogen sulfide is more pronounced at the higher temperatures than at the lower degrees of heat. Instead of a tendency of the sulfide sulfur to be converted into organic sulfur, the reverse of this seems to be true above 500°. This can be explained by the fact that very little sulfide sulfur can be formed from the small percentage of pyrite and sulfate, whereas organic sulfur is present in fairly large quantities. The reaction would seem to be reversible and an excess of one form of sulfur causes the equilibrium to shift toward the other form.

PITTSBURGH COAL—In Tables IX and X are given the results obtained for the Pittsburgh coal. This was carbonized at only two temperatures, 500° and 1000°.

TABLE IX—DISTRIBUTION OF SULFUR IN PITTSBURGH COAL, No. 18847
(Value given in per cent of original air-dried coal)

	0°	500°	1000°
Pyritic Sulfur	0.79	0.32	0.00
Sulfate Sulfur	0.23	0.00	0.00
Organic Sulfur	0.70	0.74	0.98
Sulfide Sulfur	0.00	0.23	0.16
Sulfur as H_2S	0.00	0.38	0.53
Tar Sulfur	0.00	0.05	0.05
Sulfur as CS_2	0.00	0.00	0.00
TOTAL	1.72	1.72	1.72

TABLE X—REACTIONS OCCURRING IN CARBONIZATION OF PITTSBURGH COAL (Results expressed in per cent sulfur on basis of air-dried coal)

Temperature Range ° C.	$FeS_2 = FeS + H_2S$	$MSO_4 = MS$	Organic S = H_2S	Organic S = Tar	MS = Organic S
0–500	0.47	0.23	0.15	0.05	0.24
500–1000	0.32	0.00	0.00	0.00	0.23
TOTAL	0.79	0.23	0.15	0.05	0.47

A study of these reactions reveals the fact that they do not differ essentially from those undergone by the Tennessee coal.

UPPER FREEPORT COAL—The Upper Freeport coal gave the results and reactions shown in Tables XI and XII.

TABLE XI—DISTRIBUTION OF SULFUR IN UPPER FREEPORT COAL, No. 23066
(Values given in per cent of original air-dried coal)

	0°	500°	1000°
Pyritic Sulfur	0.47	0.33	0.00
Sulfate Sulfur	0.07	0.01	0.00
Organic Sulfur	0.67	0.58	0.66
Sulfide Sulfur	0.00	0.09	0.12
Sulfur as H_2S	0.00	0.17	0.40
Tar Sulfur	0.00	0.03	0.03
Sulfur as CS_2	0.00	0.00	0.00
TOTAL	1.21	1.21	1.21

TABLE XII—REACTIONS OCCURRING IN CARBONIZATION OF UPPER FREEPORT COAL (Results expressed in per cent sulfur on basis of air-dried coal)

Temperature Range ° C.	$FeS_2 = FeS + H_2S$	$MSO_4 = MS$	Organic S = H_2S	Organic S = Tar S	MS = Organic S
0–50'	0.14	0.06	0.10	0.03	0.04
500–1000	0.33	0.01	0.06	0.00	0.14
TOTAL	0.47	0.07	0.16	0.03	0.18

In general, these reactions resemble those of the coals already described.

JOLIET COAL—Through the courtesy of Mr. J. V. Freeman, chief chemist of the central laboratory of the Illinois Steel Co., a sample of the coal as it is charged into the by-product ovens at that plant was obtained. A sample of the coke from the ovens was also obtained for comparison. This comparison is given later in the paper. The results obtained on this by-product coking coal are given in Tables XIII and XIV.

TABLE XIII—DISTRIBUTION OF SULFUR IN JOLIET COAL, No. 33945 (Values given in per cent of original air-dried coal)

	0°	500°	1000°
Pyritic Sulfur	0.26	0.12	0.00
Sulfate Sulfur	0.00	0.00	0.00
Organic Sulfur	0.56	0.44	0.49
Sulfide Sulfur	0.00	0.08	0.06
Sulfur as H_2S	0.00	0.16	0.25
Tar Sulfur	0.00	0.02	0.02
Sulfur as CS_2	0.00	0.00	0.00
TOTAL	0.82	0.82	0.82

TABLE XIV—REACTIONS OCCURRING IN CARBONIZATION OF JOLIET COAL (Results expressed in per cent sulfur on basis of air-dried coal)

Temperature Range ° C.	FeS_2 = FeS + H_2S	MSO_4 = MS	Organic S = H_2S	Organic S = Tar S	MS = Organic S
0–500	0.14	0.00	0.09	0.02	0.00
500–1000	0.12	0.00	0.03	0.00	0.07
TOTAL	0.26	0.00	0.12	0.02	0.07

The general course of reactions in this mixed coking coal resembles that of the majority of coals studied.

RAW AND WASHED VANDALIA COAL—Comparative tests were made between a coal in the raw state and the same coal after passing through a washery. The results of these tests are given in Tables XV and XVI.

TABLE XV—DISTRIBUTION OF SULFUR IN RAW VANDALIA COAL, No. 33819, AND WASHED VANDALIA COAL, No. 33821 (Values given in per cent of original air-dried coal)

	RAW			WASHED		
	0°	500°	1000°	0°	500°	1000°
Pyritic Sulfur	0.70	0.32	0.00	0.25	0.12	0.00
Sulfate Sulfur	0.03	0.00	0.00	0.03	0.00	0.00
Organic Sulfur	0.65	0.50	0.70	0.90	0.63	0.66
Sulfide Sulfur	0.00	0.12	0.11	0.00	0.04	0.03
Sulfur as H_2S	0.00	0.41	0.54	0.00	0.36	0.46
Tar S	0.00	0.03	0.03	0.00	0.03	0.03
Sulfur as CS_2	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	1.38	1.38	1.38	1.18	1.18	1.18

TABLE XVI—REACTIONS OCCURRING IN CARBONIZATION OF VANDALIA COALS (Results expressed in per cent sulfur on basis of air-dried coal)

COAL	Temperature Range ° C.	FeS_2 = FeS + H_2S	MSO_4 = MS	Organic S = H_2S	Organic S = Tar S	MS = Organic
Raw	0–500	0.38	0.03	0.22	0.03	0.10
Raw	500–1000	0.32	0.00	—0.03	0.00	0.17
TOTAL		0.70	0.03	0.19	0.03	0.27
Washed	0–500	0.13	0.03	0.29	0.03	0.05
Washed	500–1000	0.12	0.00	0.04	0.00	0.07
TOTAL		0.25	0.03	0.33	0.03	0.12

Some rather interesting comparisons can be made from these coals. In the raw coal, where the inorganic sulfur predominates, a larger quantity of metallic sulfides are converted into the organic form than in the washed coal. In the washed coal, where the organic sulfur predominates, more of the organic sulfur is decomposed into hydrogen sulfide than in the raw coal. Therefore, as might be expected, the extent to which a sulfur reaction will proceed depends very largely on the amount of the reacting constituent present.

The results obtained from the tests on these various coals check up very closely the conclusions arrived at from the series of tests on the Tennessee coal. One very noticeable exception was the Pocahontas coal in which organic sulfur was present in relatively very small quantity. Because of this there was no conversion of metallic sulfides into organic sulfur, but the reaction seemed to be the reverse of this. Exceptions of this kind may be expected where the sulfur constituents are in abnormal relation to each other.

DISTRIBUTION OF COAL SULFUR IN THE COKING PROCESS

A question which has long been of great interest to the coal and coke chemists of the country is that of the behavior of the different forms of coal sulfur during the coking process. Which is eliminated in the volatile matter in the greatest proportion—the organic sulfur or the pyritic sulfur? What conditions, if any, affect the distribution ratio of the two forms between the coke and the volatile products? The conclusions of previous investigators have varied widely on this point. Campbell believes that most of the organic sulfur remains in the coke. Parr, on the other hand, states that the organic sulfur is discharged for the most part at relatively low temperatures. M'Callum concludes that a somewhat greater percentage of the organic sulfur than of the inorganic was volatilized.

From the standpoint of coal washing, the question is an important one, since this process selectively removes the pyrite without touching the organic sulfur. If organic sulfur is volatilized in greater proportion than the pyritic sulfur, coal washing for coking coals is more efficient than the sulfur reduction in the coal would indicate. The facts are that washery men have always evaluated their practice by the sulfur and ash reduction secured, without any attention to the forms of sulfur removed. Table XVII is designed to bring out the data concerning the relation of the sulfur in the coal to that in the coke.

TABLE XVII—RELATION OF THE SULFUR FORMS OF THE COAL TO SULFUR IN THE COKE (Data based on sulfate-free coal, containing only organic and pyritic sulfur forms)

COAL	Organic Sulfur Per cent of Total S	Inorganic Sulfur Per cent of Total S	Sulfur in Coal Per cent	Sulfur in Coke Per cent	Sulfur in By-product Oven Coke Per cent
Pocahontas	85.5	14.5	0.55	0.45	....
Washed Vandalia	78.2	21.8	1.15	1.14	....
Joliet Coking	68.3	31.7	0.82	0.75	0.64
Upper Freeport	58.8	41.2	1.14	1.09	....
Tennessee	50.6	49.4	3.54	3.22	....
Raw Vandalia	48.1	51.9	1.35	1.30	....
Pittsburgh	47.0	53.0	1.49	1.51	....

It will be noted that all the data above have been calculated on the basis of sulfate-free coal. This is necessary since it is known that the sulfate form is completely retained in the coke and its presence in the calculations would obscure the essential data regarding the pyrite and organic sulfur. In freshly mined coal sulfates are normally absent.

The coals have been arranged in the table in the order of their relative content of organic sulfur, beginning with the highest proportion of organic sulfur. A careful scrutiny of the percentages of sulfur in the coals and the percentages of sulfur in the corresponding cokes will not reveal any constant difference. Furthermore, the differences between the two percentages do not vary as the proportion of organic sulfur, but seem to be entirely independent of this. These figures would seem to indicate that the total sulfur of the coal is the most important factor affecting the sulfur content of the coke, that the relative amount of sulfur forms present do not affect it materially, and that certain other factors, particularly the nature of the coal, will vary the amount of sulfur in the coke to a limited extent. That another factor, not considered up to this time, materially affects the sulfur content of coke will be shown later.

A comparison between the raw and the washed Vandalia coals shows that the sulfur reduction in the coke is not even as good as the corresponding reduction of sulfur in the coal. For all practical purposes, however, the sulfur in the two cokes is roughly proportional to the sulfur in the two coals, which strongly bears out the statement just made, namely, that the total sulfur of the coal is the main determining factor and not the relative quantity of organic and inorganic sulfur.

At the time the coking coal was obtained from the Joliet by-product plant, a sample of coke, made from this coal in the ovens, was also furnished. The sulfur analysis of this coke is given in the last column of the table. The reason for the difference in the sulfur content of the coke made in the laboratory and that made in the by-product ovens is found in a very interesting secondary coking reaction, which has been well proved, and will be described in a later paper. This reaction is one between the hydrogen of the by-product gases and the red-hot coke, which results in the formation of hydrogen sulfide and its ultimate removal from the oven. This decrease in the coke sulfur due to this secondary oven reaction would apply to all the cokes in the above table, but this increased difference between the percentage of sulfur in the coal and that of the coke would in no wise affect the conclusions reached as to the effect of the relative quantities of sulfur forms present. The comparison of these tests with actual operation is interesting, however, as showing the difference between the effect of the primary sulfur reactions, as worked out in the laboratory, and the combined effect of primary and secondary reactions as shown in the by-product coke oven.

The nature of the sulfur compounds in coke has always been a problem difficult to solve. The present investigation has brought out very little additional information on this subject. It still seems probable that the majority of the coke sulfur is organic, with a smaller quantity of iron sulfide present. The nature of this iron sulfide in coke has already been described.

Proof that a magnetic sulfide of iron existed in coke was established by the following experiment: Coke, made in the laboratory from the Joliet coking coal, was pulverized in a porcelain mortar. It was found that about one per cent of this coke could be separated from the remainder by means of a large horseshoe magnet. The magnetic portion contained 2.4 per cent, and the nonmagnetic portion 0.12 per cent of sulfide sulfur.

In other words, the magnetic portion contained twenty times the percentage of sulfide sulfur that was in the remainder. This would point to the presence in the coke of magnetic sulfide of iron or pyrrhotite. Campbell has previously indicated the presence of this substance in coke and this investigation confirms his statements, but exception is taken to his claim that pyrrhotite has the formula Fe_7S_8, the true nature of this substance having been indicated earlier in this paper. Free iron has not been detected in coke prepared under careful conditions, but has been found in large quantities in coke which has been ground in an iron or steel crusher, due solely to the erosion of the machinery.

CONCLUSIONS

Previous work has indicated that sulfur exists in coal in three typical forms—pyrite or marcasite, sulfates, and organic sulfur. A study of the changes which these forms undergo during coking has been made on a variety of coals, and the five following classes of reactions established:

1—Complete decomposition of the pyrite and marcasite to ferrous sulfide, pyrrhotite, and hydrogen sulfide. This reaction begins at 300° C., is complete at 600° C., and generally reaches its maximum between 400° and 500° C.

2—Reduction of sulfates to sulfides. This reaction is complete at 500° C.

3—Decomposition of the organic sulfur to form hydrogen sulfide. From one-quarter to one-third of the organic sulfur is so affected in the primary decomposition, but the by-product gases traveling through the coking mass increase this reaction to as much as one-half of the organic sulfur present. Primary decomposition is most active below 500° C.

4—Decomposition of a small part of the organic sulfur to form volatile organic sulfur compounds. The greater portion of these find their way into the tar. This decomposition occurs at the lower temperatures of the coking process.

5—Disappearance of a portion of the ferrous sulfide and pyrrhotite, the sulfur apparently entering into combination with the carbon. This reaction seems to be most active in the neighborhood of 500° and higher.

The organic sulfur not accounted for by the above reactions undergoes a decided change in character between 400° and 500° and shows none of the properties of the original coal sulfur.

This investigation indicates that the total sulfur of the coal is the most important factor affecting the sulfur content of the coke, that the relative amounts of sulfur forms present do not affect it materially, and that certain other factors, particularly the nature of the coal, will vary the amount of sulfur in the coke to a limited extent.

The secondary reaction between the sulfur of the red-hot coke and the hydrogen of the by-product gases traveling through it causes a more marked reduction in the amount of sulfur left in the coke than the above primary reactions would indicate.

A magnetic sulfide of iron, probably pyrrhotite, has been proved to be present in coke.

ACKNOWLEDGMENTS

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THE DESULFURIZING ACTION OF HYDROGEN ON COKE[1,2]

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Sulfur has always been an objectionable constituent of coke, and, as the supply of low sulfur coal becomes less, the presence of more and more sulfur in metallurgical coke is a real problem. Coal washing has been resorted to in many regions where high sulfur coal is mined, but even efficient methods of washing often will not solve the problems, since this treatment removes a part of the sulfur which is combined as pyrites, but does not affect the finely disseminated iron pyrite or the sulfur in organic combination.[3] In most cases, one-fourth to one-half of the sulfur in coal can be removed by washing, which means a corresponding reduction in the coke sulfur, as has been shown previously by the author.[4]

PROCESSES FOR THE DESULFURIZATION OF THE COKE

In addition to methods for removing a portion of the sulfur in coal by washing, many schemes have been proposed for the removal of sulfur from the coke itself. All of these processes involve either the elimination of the sulfur as volatile compounds or its conversion into compounds which may later be leached out with water, and which, by their nature, are harmless for the uses to which the coke is to be put. A general summary of desulfurizing processes which have been patented or proposed follows.

PROCESSES INVOLVING THE PASSAGE OF GASES THROUGH THE COKING MASS. *Steam*—Scheerer[5] in 1854 passed high pressure steam into an oven before drawing the coke, and claimed a resultant loss of 0.4 per cent sulfur in the coke. A steam desulfurizing process was patented by Claridge and Roper in 1858. Woltereck[6] has a process combining the use of air and steam at not over 400° C., by which it is claimed the sulfur is driven out as the dioxide. The disadvantage of steaming processes is that an excessive amount of the coke is used up to secure desulfurization.

Air—The passage of air through red-hot coke was investigated by Philippart.[7] Elimination of a part of the sulfur as sulfur dioxide was secured, but only at the expense of a prohibitive portion of the coke. The use of air under high pressure with the coke at 300° C. did not give very efficient desulfurization.

Chlorine—Stoner[8] has a process in which coke is treated at the close of the coking operation with chlorine or chlorinated gases, and then washed to remove the soluble salts. This process is rather expensive, and furthermore tends to destroy the coke and by-products. Fingerland[1] passes chlorine through the hot coke after adding certain catalyzers, and claims that the sulfur passes off as sulfur dichloride.

Carbon monoxide—Several patents call for the use of carbon monoxide, but no data as to their efficiency are available.

PROCESSES INVOLVING THE ADDITION OF COMPOUNDS TO THE COAL BEFORE COKING—*Salt*—In England the Calvert process[2] made use of sodium chloride added to the coal before coking. The purpose was to form volatile compounds of sulfur and phosphorus with the chlorine of the salt, but later experiments have demonstrated that sulfur is actually increased in the coke by the addition of salt. The Rowan process, patented in 1868, made use of the addition of salt, with subsequent washing of the coke by immersion in water. It is claimed that this process gave good results, but it has never been applied on a commercial scale.

Sodium carbonate—This process, patented by Spurrier,[3] is not in reality a desulfurizing process, but is simply the addition of sodium carbonate in excess, to prevent the sulfur of the coke from uniting with the iron in the smelting operation.

Manganese dioxide—The addition of manganese dioxide to coal before coking has been patented by Franck.[4] The claim is made that the oxygen liberated effects a rapid combustion of the organic sulfur compounds, which are then removed with the gases. No mention is made of the simultaneous oxidation of the coal substance proper, which must be excessive.

PROPOSED METHOD

None of the coke desulfurization processes just described have ever found extensive application, and the author knows of no large-scale operation based on any of these processes in this country. Coke desulfurization must of necessity be cheap, must remove a large percentage of the sulfur, and must involve little change in existing equipment. In addition, a successful process must not affect the quality or quantity of coke produced.

In the preceding paper the reactions which coal sulfur undergoes during carbonization have been described. From these experiments it was concluded that pyrite decomposed to form ferrous sulfide or pyrrhotite and hydrogen sulfide, the ratio between the residual sulfur and the volatile sulfur being about 1 : 1. Secondary reactions at the higher temperatures of the coking process cause the ferrous sulfide to change over partly to what is apparently a "carbon-sulfur" compound.[5] The organic sulfur completely decomposes, more than one-half being retained in the coke in an altered form, while the remainder is evolved as hydrogen sulfide, together with small quantities of thiophene or other volatile organic compounds. The resulting sulfur of the coke will consist, therefore, of iron sulfide, either as ferrous sulfide or as pyrrhotite, and a larger quantity of a very stable organic sulfur substance. The percentage of organic sulfur in the coke is higher than that of the

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[1] Published by permission of the Director of the U. S. Bureau of Mines.

[2] Presented by title at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[3] T. Fraser and H. F. Yancey, *Bull. Am. Inst. Mining Eng.*, **1919**, 1817.

[4] Alfred R. Powell, This Journal, **12** (1920), 1069.

[5] Groves and Thorp, "Chemical Technology," **1**, p. 123. J. and A. Churchill, London, **1889**.

[6] D. R. P. 261,361, May 2, 1912.

[7] Groves and Thorp, *Loc. cit.*

[8] U. S. Patent 887,145, May 12, 1908.

[1] D. R. P. 270,573, June 7, 1913.

[2] Groves and Thorp, *Loc. cit.*

[3] U. S. Patent 1,007,153, October 31, 1911.

[4] D. R. P. 274,853, April 12, 1912.

[5] References in this paper to a "carbon-sulfur" compound and to organic sulfur in coke are simply convenient terms to designate a combination or existence of sulfur in coke as yet unknown. Indications point to the association of this sulfur with the carbon of the coke, but whether this is a physical or a chemical association is as yet undetermined.

TABLE I—SOURCE AND PROXIMATE AND SULFUR ANALYSES OF COALS[1]

LABORATORY NUMBER	NAME	SOURCE	Moisture	Volatile Matter	Fixed Carbon	Ash	Sulfur
18847	Pittsburgh	Pennsylvania, Bruceton, Experimental Mine, Bureau of Mines	1.57	38.72	54.95	4.75	1.72
23066	Upper Freeport	Pennsylvania, Butler Co., Cunningham Coal Company	2.04	33.11	56.36	8.49	1.21
33945	Joliet coking	Pocahontas, 65%; Lynch, Ky., 20%; Franklin Co., Ill. (washed), 15%. As charged in by-product ovens, Illinois Steel Co., Joliet, Ill.	0.92	26.28	65.60	7.20	0.82

[1] All samples in an air-dry conditon.

inorganic sulfur; hence, the former is the substance to be attacked in a desulfurization process.

One means of accomplishing desulfurization would be to modify the sulfur reactions of the coking process so as to secure larger amounts of the volatile sulfur compounds and less of the residual. Another method would be to attack the sulfur of the finished coke in an attempt to secure its removal. The process developed in this investigation could be used in either way, but it is more convenient to apply the necessary methods during the carbonization period.

Some time ago a method was proposed for the determination of total sulfur in coke by the use of nascent hydrogen.[1] This method has never come into extensive use for the purpose for which it was intended, but is interesting as showing the comparative ease with which the stable sulfur in coke may be eliminated. The powdered coke was mixed with zinc or aluminium foil, and heated in water, and hydrochloric acid was added. Most of the sulfur was eliminated as hydrogen sulfide, although the author has never found that the method completely converts the sulfur into hydrogen sulfide.

Since nascent hydrogen has such a decided effect on the coke sulfur, it was thought that hydrogen passed through the coking mass might show a material desulfurizing action. If this were so, the process might find extensive commercial application, since the lean gases produced by the carbonization of coal contain about 50 per cent of hydrogen. Thus a by-product could be utilized for the desulfurization which would not injure the coke, and, furthermore, the by-product gas itself would not be changed essentially.

EXPERIMENTAL METHOD

All the experimental work described in this paper has been done in a very small laboratory apparatus. The process is now being applied on a larger scale, using a 10-lb. charge; if these experiments are successful, tests will be made in commercial coke ovens.

The apparatus was essentially the same as that used in the study of reactions of coal sulfur during the coking process, and fully described in the paper already referred to.

The coking charge consisted of 5 g. of coal contained in a fused silica tube. This tube was heated by an electric tube furnace with the temperature under close control at all times. Hydrogen was admitted to the inlet end of the coking tube through a flowmeter, so that the rate of flow could be maintained fairly constant. The supply of hydrogen was furnished by a Kipp generator, which gave a uniform rate of flow. The outlet end of the tube contained a cotton plug for a tar filter, and was connected to a flask containing ammoniacal cadmium chloride to collect the hydrogen sulfide evolved. At the end of the coking process the contents of the cadmium chloride flask were acidified, and the hydrogen sulfide determined iodometrically.

The coke was pulverized and treated with dilute hydrochloric acid, by which means the sulfur combined as sulfide was evolved as hydrogen sulfide, which was absorbed in cadmium chloride and titrated with iodine.

The residue from the hydrochloric acid extraction was treated with nitric acid (sp. gr. 1.12) for 24 hrs. at room temperature to extract any pyrite that might remain, then filtered, the filtrate evaporated to dryness, and sulfur and iron determined by the usual methods. By comparison of these analyses with those of the corresponding tests where no hydrogen was used, the efficiency of hydrogen as a desulfurizing agent could be estimated. In most cases the determination of the hydrogen sulfide evolved, as the measure of desulfurization, was checked by actual determination of the sulfur in the coke.

DESCRIPTION OF COALS

Three coals were used in this investigation. Table I gives the laboratory sample number, the name to be used in referring to the coal, a brief description of its source, and the results of proximate and sulfur analyses.

RESULTS OF EXPERIMENTS

PITTSBURGH COAL—The Pittsburgh coal was completely carbonized by being kept in the tube furnace for 2 hrs. at 1000°. It had been found by previous tests that the coal sulfur reaches a condition of stability under these conditions, and that no more hydrogen sulfide will be evolved by keeping the coke at this temperature for a longer period. Pure hydrogen was then passed through the furnace at the rate of 100 cc. per minute for a period of one hour.[1] Comparative figures on the coke sulfur before and after the treatment with hydrogen are given in Table II.

TABLE II—DESULFURIZATION OF COKE FROM PITTSBURGH COAL BY HYDROGEN

	Without Hydrogen	With Hydrogen
Total sulfur in coal (Per cent air-dry coal)	1.72	1.72
Sulfur evolved as hydrogen sulfide (Per cent air-dry coal	0.53	0.74
Sulfur in coke (Per cent air-dry coal)	1.14	0.93
Sulfur in coke (Per cent air-dry coke)	1.90	1.55

In interpreting these results, it must be kept in mind that the hydrogen was passed through the fin-

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[1] N. Oteha, *Z. angew. Chem.*, **1897**, 330.

[1] A flow of hydrogen of 100 cc. per minute for one hour through 5 g. of coal would mean 38 M cu. ft. per ton of coal. It must be remembered that the coal rested in the bottom of the tube in the laboratory apparatus, and the majority of the hydrogen simply passed over without accomplishing any desulfurization. For this reason there can be no comparison between laboratory conditions and actual coke-oven practice, so far as the amount of hydrogen required is concerned.

ished coke after, and not during, its formation. The sulfur analysis of this coal shows that out of the total sulfur percentage of 1.72, 0.79 per cent is combined as pyrite, 0.23 per cent as sulfate, and 0.70 per cent as organic sulfur. The large amount of sulfide sulfur in the coal accounts for the high sulfur coke from the ordinary distillation. The flow of hydrogen for one hour brought the coke sulfur from 1.90 down to 1.55 per cent.

The coke was now cooled from 1000° to 500° C., and the flow of hydrogen continued. Under these conditions, no hydrogen sulfide was obtained, showing that no desulfurization took place on the finished coke at this temperature. On raising the temperature again to 1000°, evolution of hydrogen sulfide continued at the same rate as before.

Tests on the Pittsburgh coal were continued and the hydrogen was passed through continuously from the start of the carbonization, at a rate of 100 cc. per minute. After 2 hrs. at 500°, it was found that 1.6 times as much hydrogen sulfide had been evolved as in a corresponding test without the use of hydrogen. The charge was then slowly carried up to 1000° over a period of 2 hrs. Table III shows the effect of the 4 hr. flow of hydrogen, as compared with a coking test where no hydrogen was used.

TABLE III—DESULFURIZATION BY HYDROGEN IN COKING TEST OF PITTSBURGH COAL

	Without Hydrogen	With Hydrogen
Total sulfur in coal (Per cent air-dry coal)......	1.72	1.72
Sulfur evolved as hydrogen sulfide (Per cent air-dry coal)............	0.53	1.15
Sulfide sulfur in coke (Per cent air-dry coal)....	0.16	0.08
Total sulfur in coke (Per cent air-dry coal)....	1.14	0.52
Total sulfur in coke (Per cent air-dry coke)....	1.90	0.86

Actual analysis of the sulfur in the coke checked within a few hundredths of a per cent with that given above by difference. The result of this experiment was a reduction of sulfur in the coke from 1.90 to 0.86 per cent, or a decrease of considerably over one-half. This reduction was obtained from a coal containing sulfur of a very nonvolatile nature, as shown by the high sulfur content of the coke as compared with the coal.

Further experiments with the Pittsburgh coal in which the hydrogen was mixed with a small quantity of moist hydrochloric acid vapor gave results agreeing closely with those given above. As a matter of fact, the total sulfur in this coke was a little higher than in the coke from the straight hydrogen run, although the sulfide sulfur was a little lower. The addition of a small quantity of hydrochloric acid vapor cannot, therefore, be regarded as assisting desulfurization.

UPPER FREEPORT COAL—Two runs were made to determine the effect of hydrogen on the desulfurization of the Upper Freeport coal. One of these was made at 500° for 2 hrs. with the hydrogen flowing at the rate of 100 cc. per minute. The other was made at 500° for one hour, and then at 1000° for an hour, with the hydrogen flow at 100 cc. per minute. This latter run was made with the hydrogen slightly moist, since this seems to favor desulfurization. Analyses of the products were made by the methods described in the previous paper.[1] A summary of the results, together with the corresponding results obtained without the use of hydrogen, is given in Table IV.

TABLE IV—DISTRIBUTION OF SULFUR WITH AND WITHOUT HYDROGEN IN UPPER FREEPORT COAL, No. 23066

(Values given in per cent of original air-dry coal)

		Without Hydrogen		With Hydrogen	
	Coal	500° C.	1000° C.	500° C.	1000° C.
Pyritic sulfur........	0.47	0.33	0.00	0.01	0.00
Sulfate sulfur........	0.07	0.01	0.00	0.01	0.00
Organic sulfur.......	0.67	0.58	0.66	0.63	0.07
Sulfide sulfur........	0.00	0.09	0.12	0.17	0.00
Sulfur evolved as H_2S	0.00	0.17	0.40	0.36	1.11
Tar sulfur...........	0.00	0.03	0.03	0.03	0.03
Total sulfur.........	1.21	1.21	1.21	1.21	1.21

The sulfur left in the coke at 1000° is the sum of the organic sulfur and the sulfide sulfur. If the percentages given above on the basis of the original coal are figured to the percentage of sulfur in the coke, the coke produced without hydrogen contains 1.20 per cent sulfur, while the coke made with the hydrogen contains 0.11 per cent sulfur. There has therefore been a reduction of over 90 per cent of the coke sulfur due to the effect of the hydrogen. This was the highest reduction obtained by the use of hydrogen during the coking process. The passage of the hydrogen seemed to produce no effect on the character of the coke, other than to remove the sulfur, although the coke produced from this coal was rather fragile and crumbly both with and without hydrogen treatment.

From the data given in Table IV, the reactions which the various forms of sulfur had undergone during the coking process were calculated on a basis which has been discussed in the previous paper. The figures (in Table V) to express the magnitude of the reactions are in terms of per cent of sulfur reacting, on the basis of the weight of the original air-dried coal.

TABLE V—REACTIONS OCCURRING IN CARBONIZATION OF UPPER FREEPORT COAL

(Results expressed in per cent sulfur on basis of air-dry coal)

Temperature Range, ° C.	$FeS_2 = FeS + H_2S$	$MSO_4 = MS$	Organic S $= H_2S$	Organic S = Tar S	MS = Organic S
		WITHOUT HYDROGEN			
0–500	0.14	0.06	0.10	0.03	0.04
500–1000	0.33	0.01	0.06	0.00	0.14
		WITH HYDROGEN			
0–500	0.46	0.06	0.13	0.03	0.12
500–1000	0.01	0.01	0.88	0.00	0.18

A study of Table V shows that three of the five reactions are modified by the presence of hydrogen. The coal pyrite is caused to decompose at a lower temperature, the decomposition being practically complete at 500°; whereas without the hydrogen, less than one-third of the sulfur had been affected below 500°. This was to be expected, since the speed of decomposition of pyrite is determined not only by the temperature, but also by the partial pressure of free sulfur over it. The presence of an excess of hydrogen keeps the amount of free sulfur down to an almost negligible quantity. It should be pointed out here that the modification of this pyrite decomposition reaction does not assist the desulfurization process directly, since no more sulfur elimination is secured than in the case of ordinary distillation, but this sulfur elimination occurs during an earlier stage of the carbonization.

The entire desulfurizing effect of the hydrogen is due to the increased conversion of organic sulfur into hydrogen sulfide. A comparison of the figures on this

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[1] *Loc. cit.*

reaction shows that below 500° the increased elimination of sulfur due to the hydrogen is very slight, but that above 500° the difference is enormous. This bears out the conclusions reached previously, namely, that desulfurization by hydrogen is most active at the higher temperatures of the coking process.

The third reaction affected by the passage of hydrogen through the coking mass is the fixing of the sulfide sulfur in some combination with carbon or coke substance. The changes in the extent of this reaction are secondary and are not caused directly by the hydrogen, but are due to a mass-action effect. Below 500° hydrogen causes an increased decomposition of pyrite, thus making an increased amount of ferrous sulfide, which by mass action increases the extent of this particular reaction. Above 500° the constant elimination of the organic sulfur as hydrogen sulfide also tends to increase the extent of the reaction by decreasing the resulting product of the reaction.

This conversion of the sulfide sulfur into a "carbon-sulfur" combination must be regarded as of considerable assistance in the desulfurization process, although it in itself does not cause the elimination of sulfur from coke. Hydrogen does not react with hot ferrous sulfide[1] although it will react very readily with the "carbon-sulfur" combination of the coke. This reaction, therefore, carries the ferrous sulfide to an easily eliminated form of sulfur.

USE OF BY-PRODUCT GAS—The experiments so far described have been carried out with pure hydrogen. Since any possible practical use of the process would be carried out with the by-product gas from the coking operation, it was desired to determine the desulfurizing effect of such a gas. The gas made for this purpose had the following approximate composition by volume.

	Per cent
Hydrogen	50.0
Methane	25.0
Carbon monoxide	15.0
Air, CO_2, etc.	10.0
TOTAL	100.0

This gas, which corresponds very closely to an average lean coke-oven gas, at least in the content of hydrogen, was passed through the Upper Freeport coal at the same rate and under exactly the same conditions as the hydrogen had been. The results are given in Table VI, together with comparative results from the ordinary distillation, and the distillation with pure hydrogen.

TABLE VI—SULFUR ELIMINATED AND SULFUR RETAINED IN COKE UNDER DIFFERENT CONDITIONS OF DISTILLATION—UPPER FREEPORT COAL

(Total sulfur 1.21 per cent)

	Sulfur Eliminated as H_2S (Per cent on Basis of Air-Dry Coal)				Sulfur in Coke
	1 hr.	1.5 hrs.	2 hrs.	3 hrs.	Per cent
Ordinary distillation	0.17	....	0.40	....	1.20
By-product gas purge	0.40	....	0.86	0.96	0.34
Hydrogen purge	0.72	1.02	1.11	....	0.11

The elimination of hydrogen sulfide under the different conditions of distillation is shown graphically in Fig. 1. From these comparative results it appears that a 50 per cent hydrogen mixture is much slower in its desulfurizing action, and in practice would never reach the degree of desulfurization attained by the pure hydrogen. Nevertheless, the sulfur removal by the by-product gas is decided, as shown by the reduction in coke sulfur from 1.20 per cent to 0.34 per cent.

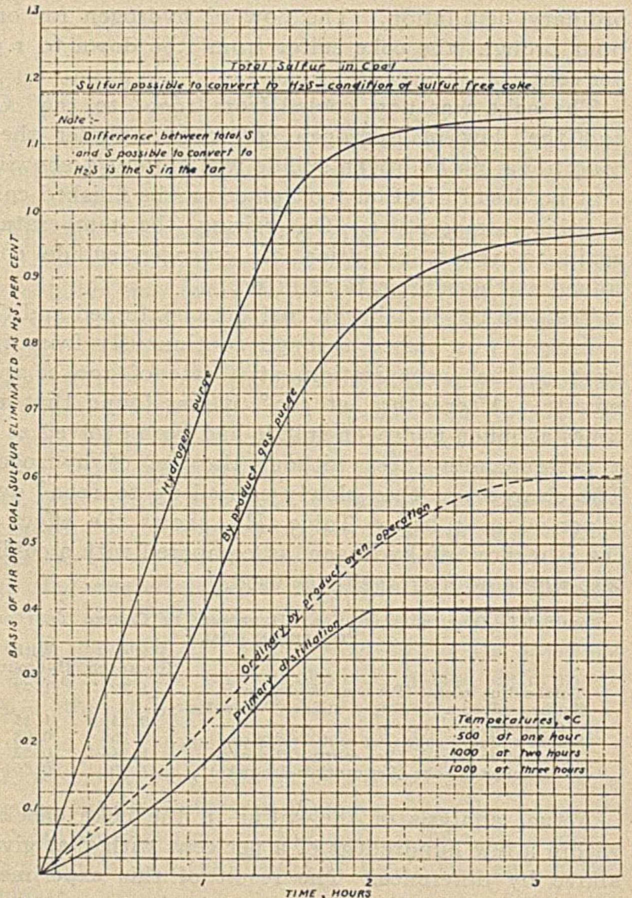

FIG. 1—CURVES SHOWING ELIMINATION OF SULFUR AS HYDROGEN SULFIDE FROM UPPER FREEPORT COAL, NO. 23066, WHEN COKED UNDER DIFFERENT CONDITIONS. IN PRIMARY DISTILLATION NO HYDROGEN-CONTAINING GAS IS PASSED THROUGH

JOLIET COKING COAL—In Table VII are given the data on the passage of hydrogen through the Joliet coking coal for a 3-hr. period. This run differed from the others in that the coal was not pulverized to 100-mesh size, but was of mostly 10-mesh size.

TABLE VII—DESULFURIZATION BY HYDROGEN IN COKING TEST OF JOLIET COAL

	Without Hydrogen	With Hydrogen
Total sulfur in coal (Per cent air-dry coal)	0.82	0.82
Sulfur as hydrogen sulfide (Per cent air-dry coal)	0.25	0.59
Total sulfur in coke (Per cent air-dry coal)	0.55	0.21
Total sulfur in coke (Per cent air-dry coke)	0.75	0.29

It is to be noted that the sulfur of the coke was reduced from 0.75 to 0.29 per cent, even with the coal in comparatively coarse granules. Another run with the coal ground to 100 mesh did not show even as good sulfur elimination as the coarser size. Since the coal has entirely fused into one mass at the temperatures at which desulfurization takes place (500° to 1000°), the state of subdivision of the original coal should not affect the desulfurizing process materially.

The coke made from the Joliet coking coal as produced in the by-product ovens contains 0.64 per cent

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[1] Roscoe and Schlorlemmer, "Treatise on Chemistry," Macmillan & Co., London, **1907**, Vol. II, p. 1208.

sulfur. The coke made in the laboratory from the same coal contains 0.75 per cent sulfur, the difference being due to the purging effect of the by-product gases passing through the red-hot coke in the oven. A test, to determine how much the finished coke from the by-product oven could be desulfurized by heating to 1000° and passing hydrogen through for one hour, resulted in a reduction in the coke sulfur from 0.64 to 0.50 per cent, showing that desulfurization of coke by hydrogen was not limited to the actual coking process.

CONCLUSIONS

A study has been made of the efficiency of hydrogen and gases containing hydrogen as desulfurizing agents, when passed through finished coke at high temperatures or through coal in the process of coking.

The effect of hydrogen on the removal of sulfur from coke is very noticeable, in most cases the majority of the sulfur being removed during a period of 3 hrs. at 1000° C. With the exception of the decrease in sulfur content, the character of the coke does not seem to be affected by the passage of hydrogen.

Three of the sulfur coking reactions are modified by the passage of hydrogen through the coking mass.

(1) Coal pyrite, FeS_2, is caused to decompose at a lower temperature, the decomposition being practically complete at 500°. This change of speed of reaction does not affect the final desulfurization results, however, since complete decomposition of the pyrite is finally attained in the ordinary coking process.

(2) The decomposition of organic sulfur to form hydrogen sulfide is very little affected below 500°, but is enormously increased from 500° to 1000°. All of the desulfurizing effect of the hydrogen is due to this increased decomposition.

(3) A larger amount of sulfide is converted to a "carbon-sulfur" combination. This is due to mass action and results from the modifications in the two reactions given above.

Gaseous mixtures containing hydrogen, such as coke-oven gas, are slower in their desulfurizing action, and even with a longer time of exposure would probably never give the degree of desulfurization attained by the use of pure hydrogen. Their efficiency for the removal of sulfur from coke is high, however, and the repassing of by-product gas through the coking mass may prove of commercial value.

The original state of subdivision of the coal does not affect the desulfurization process. This is because the coal fuses between 350° and 400°, while desulfurization begins above 500°.

The coke produced in coke ovens contains less sulfur than would be accounted for by the primary coking reactions. This is due to the flow of the by-product gas produced through the coking mass.

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NAPHTHALENE SULFONIC ACIDS. I—SOME DIFFICULTLY SOLUBLE SALTS OF CERTAIN NAPHTHALENE SULFONIC ACIDS[1]

By Joseph A. Ambler[2]

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In the course of the investigation of the sulfonation products of naphthalene, it became of interest to make and study as many as possible of the more difficultly soluble salts of those acids which might be formed by direct sulfonation, *viz.*, the α- and β-monosulfonic acids and the 1,5-, 1,6-, 2,6- and 2,7-disulfonic acids of naphthalene. The purpose of investigating these salts was to obtain a characteristic salt of each acid which might serve as the basis of a qualitative test for that acid.

The known difficultly soluble inorganic salts of these acids were found unsuited for the purpose in hand, with the exception of the salts of naphthalene-β-sulfonic acid with the heavier metals; such as the nickel, cobalt, copper, cadmium, zinc, and silver salts described by O. N. Witt,[3] and the ferrous salt,[4] known in the industries but not described in any scientific work so far as the author can find.

Erdmann and Süvern[5] are the only ones who have recorded work on the salts of these acids with organic bases. They describe the salts of the α-, β-, 2,6- and 2,7-sulfonic acids with aniline, benzidine, and *o*-tolidine, but give no analyses of the salts formed.

To investigate this class of salts more thoroughly, salts of various organic bases with the six sulfonic acids were prepared, and those that were difficultly soluble were studied further. The most important of these are described here, and some of their uses in the following paper. Other difficultly soluble salts will probably be described in later contributions from this laboratory.

The method of making the salts was the same in each case. Molecularly equivalent quantities of the acid, or its sodium or potassium salt, and the hydrochloride of the organic base were dissolved separately in hot water, and the two solutions mixed, stirred thoroughly, and allowed to cool. The crystallized salts were filtered, washed with cold water, and dried in a vacuum oven at 100°.

Since they are salts of strong acids with weak bases, they are all easily hydrolyzed by boiling water. In attempting to recrystallize them, a little of the hydrochloride of the base should always be added to counteract this change.

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

[2] Crystallographic-optical data by Edgar T. Wherry.

[3] *Ber.*, **48** (1915), 743.

[4] Cain, "Manufacture of Intermediate Products for Dyes," p. 166; Brit. Patent 4459 (1894).

[5] *Ann.*, **275** (1893), 297.

The sulfur in all of these salts was determined as follows: An amount of the salt not exceeding 200 mg. was ignited in a Parr calorimeter bomb with about 5 g. of sodium peroxide. The ignition mass was dissolved in water, the solution acidified, and sulfuric acid was determined as usual by precipitation with barium chloride.

α-NAPHTHYLAMINE NAPHTHALENE-α-SULFONATE,

$C_{10}H_7NH_2.C_{10}H_7SO_3H$

This salt separates, on cooling the hot solution, in well-defined, glistening, micaceous leaflets, generally arranged in groups. It is soluble in hot water, in hot 95 per cent alcohol, and in a cold mixture of 4 volumes of alcohol and 1 of water, but is practically insoluble in cold water and alcohol and in acetone. It melts with decomposition at 232°. Upon analysis, 9.09 and 9.34 per cent of sulfur were found, with the calculated value at 9.13 per cent.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES.[1] *Crystal habit*—When examined under the microscope in ordinary light seen to be made up of overlapping plates.

Refractive indices (for D)—[Determined by inserting the polarizer (sub-stage nicol prism) and immersing a small amount of the substance on a microscope slide in liquids of known refractive index one after another until the crystals lying in some definite position disappear, because their index is matched; and repeating for crystals lying in other positions.]

$\alpha = 1.552$, β not determined, $\gamma = 1.795$, $\gamma - \alpha = 0.243$, all ± 0.005; indices α and γ usually shown.

Features shown in parallel polarized light, with nicols crossed—Double refraction extreme, the colors being first to second order, often in beautiful mosaics, on thin plates, but ranging up to fourth or fifth order on thick or upturned ones; extinction parallel to occasional edges; elongation indefinite.

Features shown in convergent polarized light, with nicols crossed—None.

Diagnostic features—The features likely to be of greatest use in identifying this substance are the crystal habit and the value of the lowest refractive index, α. If immersed in nitrobenzene ($n_D = 1.552$) or another oily liquid with about the same n, and examined under the microscope with the polarizer in, the plates disappear practically completely when the direction of index α lies parallel to the plane of vibration of the polarizer.

β-NAPHTHYLAMINE NAPHTHALENE-α-SULFONATE,

$C_{10}H_7NH_2.C_{10}H_7SO_3H$

This salt crystallizes on cooling from dilute hot solutions in large, glistening, micaceous, diamond-shaped plates. If the hot solution is too concentrated, it forms on cooling a stiff jelly resembling slightly cooked egg albumen. This jelly-like form may partially change, on standing, into a mass of long colorless needles. If this jelly-like form is heated with more water, it dissolves, and the plates are formed on cooling.

The plates are difficultly soluble in cold water, acetone, and 95 per cent alcohol; but soluble in hot water, hot acetone, hot alcohol, and in a cold mixture of 4 volumes of alcohol and 1 of water. The salt blackens at 202° and melts at 211°. Analyses gave 9.08 and 8.98 per cent sulfur (theory, 9.13).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Elongated plates, sometimes showing a 125° termination.

Refractive indices (D)—$\alpha = 1.620$, $\beta = 1.670$, $\gamma =$ greater than 1.850, $\gamma - \alpha = 0.23+$, all ± 0.005; indices α and β are usually shown.

In parallel polarized light—Double refraction extreme, the colors being first to second order, sometimes in confused mosaics, on thin plates; extinction parallel to prominent edges; elongation +.

In convergent polarized light—A biaxial figure frequently shown, the sign being + and $2\,E = 85° \pm 5°$.

Diagnostic features—The features most useful for identifying this substance are the crystal habit, value of the intermediate index, β, and sign of elongation. The immersion liquid may best consist of a mixture of 5 parts α-monobromonaphthalene with 1 part methylene iodide. When crystals are turned so that their longest dimension lies parallel to the plane of vibration of the polarizer, they disappear in this liquid, showing their elongation to be + in sign and the index to be 1.670.

α-NAPHTHYLAMINE NAPHTHALENE-β-SULFONATE,

$C_{10}H_7NH_2.C_{10}H_7SO_3H$

This salt forms a voluminous white precipitate in the hot solution, which is made up of microscopic needles. It is soluble in a cold mixture of 4 volumes of alcohol and 1 of water, considerably soluble in hot water and hot 95 per cent alcohol, difficultly soluble in cold water, cold 95 per cent alcohol, and hot and cold acetone. It melts with decomposition at 240° to 242°. The per cent of sulfur found was 9.08 and 9.29 (theory, 9.13).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Needles.

Refractive indices (D)—$\alpha = 1.600$, $\beta = 1.650$, $\gamma = 1.725$, $\gamma - \alpha = 0.125$, all ± 0.005; index γ usually shown lengthwise, and means of α and β crosswise.

In parallel polarized light—Double refraction extreme, bright first order colors being shown even on very minute grains; extinction parallel; elongation +.

In convergent polarized light—........

Diagnostic features—The features most useful in identifying this substance are the crystal habit, value of highest index, and sign of elongation. The immersion liquid may best consist of a mixture of 5 parts methylene iodide with 1 part α-monobromonaphthalene. When the needles are turned so that their long dimension lies parallel to the plane of vibration of the polarizer, they disappear in this liquid, showing their elongation to be + in sign and the highest index to be 1.725.

β-NAPHTHYLAMINE NAPHTHALENE-β-SULFONATE,

$C_{10}H_7NH_2.C_{10}H_7SO_3H$

This salt also forms insoluble microscopic plates in the hot solution. It is slightly soluble in hot water and 95 per cent alcohol, considerably soluble in a cold, and easily soluble in a hot mixture of 4 volumes of alcohol and 1 of water, slightly soluble in cold alcohol, and difficultly soluble in cold water and in acetone. It melts with decomposition at 276° to 279°. It contained 9.00 and 9.10 per cent of sulfur (theory 9.13).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Minute plates (or rods), with irregular wavy structure.

Refractive indices (D)—$\alpha = 1.640$, $\beta = ?$, $\gamma = 1.730$, $\gamma - \alpha = 0.090$, all ± 0.005; index α usually shown in one direction.

In parallel polarized light—Double refraction extremely strong, first to second order colors being shown even on very minute plates; extinction and elongation indeterminate.

In convergent polarized light—Traces of a biaxial figure occa-

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[1] The authors herewith acknowledge the aid of Mr. George L. Keenan of this Bureau in checking some of these data.

sionally shown, but the crystals are too minute for its measurement.

Diagnostic features—The feature most useful in identifying this substance is the unusually high value of the lowest index, α. This index is almost exactly matched by α-monochloronaphthalene (n_D = 1.639), and most of the crystals disappear in one direction or another when immersed in this liquid. For confirmative purposes the other indices may be determined in similar manner, using mixtures of this liquid with methylene iodide of the indices above stated.

FERROUS NAPHTHALENE-β-SULFONATE, $Fe(C_{10}H_7SO_3)_2.6H_2O$[1]

The author makes no claim to the discovery of this salt which has been extensively made and used in industrial plants. A description of it is given here, since no reference has been found in scientific literature or elsewhere than in the British patent.

The salt separates in large, glistening, colorless, micaceous plates, when ferrous chloride is added to a cold solution of naphthalene-β-sulfonic acid or its salts. It is difficultly soluble in cold, but readily soluble in hot water. It is remarkably stable, not being oxidized to any appreciable extent by exposure to air. At 150° to 160° all the water of crystallization is removed and the salt becomes yellowish brown, probably due to slight superficial oxidation of the iron.

Analysis	Calculated Per cent	Found Per cent	
Iron	9.67	9.52	9.53
Water	18.69	18.50	....

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Plates, sometimes showing a 140° termination.

Refractive indices (D)— α = 1.500, β not determined, γ = 1.660, $\gamma - \alpha$ = 0.160, all ±0.005; indices α and γ usually shown.

In parallel polarized light—Double refraction extreme, second order colors being shown even on thin plates; extinction parallel to crystal edges occasionally present; elongation indeterminate.

In convergent polarized light—Partial biaxial figure occasionally shown, the axial angle being large and the sign apparently +.

Diagnostic features—The feature most characteristic of this substance is the unusually low value of the lowest index, α. The immersion liquid may be benzene (n_D = 1.499), or another liquid of about the same n (for instance, some grades of lubricating oil). Most of the crystals disappear in one direction or another when immersed in this liquid. The other properties may be used for confirmation.

α-NAPHTHYLAMINE NAPHTHALENE-1,5-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt is almost completely insoluble in boiling water. It forms a heavy precipitate of a poorly defined, granular, platy nature. It is very slightly soluble in hot water, 95 per cent alcohol, and a mixture of 4 volumes of alcohol and 1 of water, and practically insoluble in these solvents in the cold, and in acetone. It does not melt below 280°. Analyses gave 10.94 and 10.97 per cent sulfur (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Plates, irregular in outline.

Refractive indices (D)— α = 1.600, β not determined, γ = 1.795, $\gamma - \alpha$ = 0.195, all ±0.005; indices α and γ often shown.

In parallel polarized light—Double refraction extreme, second order colors being shown even on very thin plates; extinction apparently inclined; elongation indeterminate.

In convergent polarized light—Partial biaxial figures rarely shown.

Diagnostic features—The value of the lowest refractive index, α, is characteristic of this substance, when considered in connection with its habit. One other compound in the series studied, α-naphthylamine naphthalene-β-monosulfonate, has the same α value, but it crystallizes in needles, and is thus readily distinguishable. For immersion, a mixture of equal parts of bromobenzene and α-monochloronaphthalene (n_D = 1.600) may be used. The crystals will disappear in one direction or another in this liquid.

β-NAPHTHYLAMINE NAPHTHALENE-1,5-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt precipitates from the boiling solution in a dense voluminous mass of small plates. It is only slightly soluble in hot water and alcohol, and practically insoluble in cold solvents, being slightly more soluble in mixtures of 4 volumes of alcohol and 1 of water. It does not melt below 280°. The results of sulfur determinations were 11.12 and 11.23 per cent (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES—Unless care is taken to have an excess of base present, there is a strong tendency for another substance, apparently an acid salt, to crystallize out along with this compound. It has so far been impossible to obtain this other substance in a pure form and no analytical data can be given at present. The acid salt has highly distinctive optical properties, and can be readily recognized when studied under the microscope, but if the two are intimately mixed difficulties may be encountered in confirming the identity of the normal salt. The properties of both are here given.

Normal salt. Crystal habit—Plates, irregular in outline.

Refractive indices (D)— α = 1.631, β = 1.647, γ = 1.755, $\gamma - \alpha$ = 0.124, all ±0.005; indices α and β are usually shown, but γ is exhibited on uptilted plates.

In parallel polarized light—Double refraction extreme, bright first order colors being shown on extremely thin plates; extinction and elongation indeterminate.

In convergent polarized light—Biaxial figures frequently shown, the sign being +, and 2 E = 75° ±5° (2 E calculated from ns = 77° 06′).

Diagnostic features—The features most useful in identifying this substance are the values of the two lower refractive indices, α and β, and the readiness with which an interference figure can be obtained. In a mixture of 3 parts α-monobromonaphthalene with one part monobromobenzene (n_D = 1.632) practically all of the plates disappear in one direction or the other; and in pure α-monobromonaphthalene (n_D = 1.656) they also disappear. On introducing the substage condenser, using a 4 mm. objective, crossing the nicol prisms, and removing the eyepiece, a fairly distinct biaxial interference figure will usually be seen, the dark brushes lying well within the field. If the microscope is provided with means for measuring axial angles, the numerical value can be obtained; if not, repetition of the procedure, using a thin flake of muscovite mica, will give a figure of practically identical dimensions, showing the axial angle to be not far from 75°.

Acid salt—This is distinguished from the normal salt by the extraordinarily strong double refraction, which exceeds 0.30, the value of α being 1.550, and that of γ being higher than the highest immersion liquid available, the n of which is 1.850. (β = 1.700.) As a result, the plates of this substance show third or fourth order colors, even when very thin. The axial angle, 2 E, is also much larger than is that of the normal salt, so that

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[1] Boulton, Haywood, Boulton, and Fergusson, Brit. Patent 4459 (1894).

the dark brushes do not appear in the field of view when the interference figure lies in the diagonal position. These features differentiate this acid salt not only from the corresponding normal salt, but also from all other compounds of the series here studied; and the acid salt, if obtained, can therefore be recognized and excluded from consideration promptly.

α-NAPHTHYLAMINE NAPHTHALENE-1,6-DISULFONATE,

$(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt separates in long, slender needles on cooling a hot solution. It is soluble in hot water, 95 per cent alcohol, soluble in cold mixtures of 4 volumes of alcohol and 1 of water, slightly soluble in cold alcohol, and practically insoluble in cold water and in acetone. It decomposes at 265° to 267°. The value found for sulfur was 11.25 and 11.22 per cent (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Well-defined rods, probably belonging to the monoclinic system.

Refractive indices (D)—$\alpha = 1.583$, $\beta = 1.730$, $\gamma = 1.770$, $\gamma - \alpha = 0.187$, all ± 0.005; index α is usually shown lengthwise, and γ crosswise, of the rods; β is sometimes shown crosswise, especially on rods so turned as to show parallel extinction.

In parallel polarized light—Double refraction extreme, the colors being second to third order, even on fairly slender rods; extinction inclined, at an angle of 17° ± 1°; elongation negative.

In convergent polarized light—Partial biaxial figure occasionally shown, the sign being —, and 2 E large.

Diagnostic features—The features most useful in identifying this substance are the value of the lowest refractive index, α, and the inclined extinction seen in parallel polarized light, with the nicol prisms crossed. The immersion liquid may consist of aniline, which has $n_D = 1.585$, which lies so near to the value of α for this substance that the rods disappear practically completely when immersed in it and turned to the appropriate position. To determine how they should lie in order that this effect shall be shown, each rod should first be examined under crossed nicols, and the stage turned until extinction occurs. If the stage is graduated, this will be found to be the case when the crystal lies at about 17° from parallelism with one or the other cross hair. On throwing out the analyzer, the rods lying near the cross hair indicating the plane of vibration of the polarizer will disappear.

β-NAPHTHYLAMINE NAPHTHALENE-1,6-DISULFONATE,

$(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt forms long, flat, silky needles when crystallized from hot water. It is soluble in hot water, 95 per cent alcohol, slightly soluble in cold alcohol, and practically insoluble in cold water and in acetone. It is soluble in a cold mixture of 4 volumes of alcohol and 1 volume of water. It does not melt below 280°. On analysis it gave 10.97 and 11.03 per cent sulfur (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Needles.

Refractive indices (D)—$\alpha = 1.550$, $\beta = 1.700$, $\gamma = 1.755$, $\gamma - \alpha = 0.205$, all ± 0.005; index α usually shown lengthwise, and means between the others crosswise of the needles.

In parallel polarized light—Double refraction extreme, the colors being third or fourth order even on slender needles; extinction parallel; elongation negative.

In convergent polarized light—Partial biaxial figures sometimes shown, the sign being apparently —, and 2 E large.

Diagnostic features—The features most useful in identifying this substance are the habit, the value of the lowest refractive index, α, and the extinction. None of the other members of the β-naphthylamine series studied crystallize in needles, although one (the 2,7-compound) is, to be sure, in rods; but this other substance differs sharply in the other two respects mentioned. The immersion liquid may best consist of nitrobenzene, or other oily liquid with n_D around 1.55. The needles disappear completely when immersed in this liquid and turned so that their long direction lies parallel to the plane of vibration of the polarizer. They also extinguish in the same position when the analyzer is inserted. The rods of the 2,7-compound, on the other hand, do not disappear in this liquid, and extinguish when lying at an angle of about 10° with a cross hair.

α-NAPHTHYLAMINE NAPHTHALENE-2,6-DISULFONATE,

$(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt separates in minute needles and lumps when a hot solution is cooled. It is moderately soluble in hot water, slightly soluble in hot 95 per cent alcohol, and practically insoluble in cold water and alcohol and in acetone. It is slightly soluble in cold alcohol diluted with one-quarter its volume of water, and soluble in the same solvent when hot. It does not melt below 280°. Analysis gave 11.07 and 11.31 per cent sulfur.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Rounded grains, in part elongated and rod-like.

Refractive indices (D)—$\alpha = 1.583$, $\beta = 1.640$, $\gamma = 1.690$, $\gamma - \alpha = 0.107$, all ± 0.005; intermediate values are usually shown.

In parallel polarized light—Double refraction extremely strong, the colors being second to third order on small grains; extinction inclined, but angle not definitely determinable; elongation variable.

In convergent polarized light—Partial interference figure occasionally shown, the sign being apparently negative, and 2 E large.

Diagnostic features—The most characteristic feature of this substance is the value of the highest refractive index, γ. On immersion in a mixture of 3 parts α-monobromonaphthalene with 2 parts of methylene iodide ($n_D = 1.689$), grains so situated as to exhibit index γ will disappear in one direction or the other. Index α is also fairly distinctive, when taken in connection with the crystal habit; for the other member of this series with the same value of α, the α-1,6-compound, is markedly rod-like in habit. Aniline ($n_D = 1.585$) is an immersion liquid coming near to the value of α in refractive index, and disappearance will occur in this liquid in the case of grains lying in the proper direction.

β-NAPHTHYLAMINE NAPHTHALENE-2,6-DISULFONATE,

$(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt forms a dense precipitate of microscopic plates (sometimes needle-like) which are only slightly soluble in hot solvents, and practically insoluble in the cold. It does not melt when heated to 280°. The per cents of sulfur found were 11.02 and 11.02.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Plates, with a more or less rhombic outline.

Refractive indices (D)—$\alpha = 1.610$, $\beta = 1.634$, $\gamma = 1.830$, $\gamma - \alpha = 0.220$, all ± 0.005; indices α and β are usually shown, γ appearing only on uptilted plates.

In parallel polarized light—Double refraction extreme, the colors being first to second order on very thin plates; extinction inclined at large angles, up to 40°, with respect to crystal edges often present, but parallel to the edges of uptilted plates; elongation variable on the usual plates, — on the uptilted ones.

In convergent polarized light—An interference figure frequently shown, the sign being +, and 2 E = 70° ± 5° (2 E calculated from $ns = 76° 26'$).

Diagnostic features—The habit of this substance is characteristic, and, when taken in connection with the indices as listed, renders the identification of the substance an easy matter. The lowest refractive index, α, is approximately matched by a mixture of equal parts of monobromobenzene and α-monochloronaphthalene (n_D = 1.600), and the intermediate one, β, by α-monochloronaphthalene (n_D = 1.640).

α-NAPHTHYLAMINE NAPHTHALENE-2,7-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt separates very slowly in the form of groups of long needles, when the hot solution is cooled. It is soluble in hot water, in hot and cold 95 per cent alcohol, and in cold alcohol diluted with one-quarter of its volume of water, but practically insoluble in cold water and in acetone. It decomposes gradually without melting when heated above 220°. It gave on analysis 11.01 and 11.24 per cent sulfur (theory 11.16).

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Rods, the more slender ones slightly curved.

Refractive indices (D)— α = 1.560, β = 1.650, γ = 1.675, $\gamma - \alpha$ = 0.115, all ±0.005; index α usually shown lengthwise, and means of the others crosswise.

In parallel polarized light—Double refraction extreme, the colors being third order on even slender rods; extinction parallel; elongation —.

In convergent polarized light—Partial biaxial figure rarely shown, the sign being +.

Diagnostic features—The features most useful in identifying this substance are the value of the lowest refractive index, α, and the parallel extinction. Monochlorobenzene (n_D = 1.561) matches the index in question, and the rods disappear when their long direction lies parallel with the plane of vibration of the polarizer. Between crossed nicols the extinction is parallel, a property which distinguishes this compound sharply from the one likely to be confused with it, the 1,6-disulfonate.

β-NAPHTHYLAMINE NAPHTHALENE-2,7-DISULFONATE, $(C_{10}H_7NH_2)_2.C_{10}H_6(SO_3H)_2$

This salt forms a mass of long, slender needles on cooling a hot solution. It is soluble in hot water and 95 per cent alcohol, practically insoluble in cold water and alcohol and in acetone, and appreciably soluble in a cold mixture of 4 volumes of alcohol and 1 of water. It does not melt when heated to 280°. Analysis gave 11.07 and 11.16 per cent sulfur.

CRYSTALLOGRAPHIC-OPTICAL PROPERTIES. *Crystal habit*—Rods, in part plate-like; sometimes showing a 130° termination; often twinned, that is, grown together in groups of two in definite crystallographic relationship.

Refractive indices (D)— α = 1.530, β = 1.700, γ = 1.740, $\gamma - \alpha$ = 0.210, all ±0.005; index α is often shown lengthwise on the twins, but crosswise on rods with parallel extinction; β is shown lengthwise on the latter.

In parallel polarized light—Double refraction extreme, colors being second or third order even on thin plates, down to first on parallel-extinguishing rods; extinction inclined, on twins making an angle of 8° ± 1° with the twinning plane, often parallel on untwinned rods; elongation variable, but usually + on untwinned rods.

In convergent polarized light—A biaxial interference figure often shown, the obtuse bisectrix being perpendicular to the plates; 2 E is evidently large and sign —.

Diagnostic features—The features most useful for identifying this substance are the habit, especially the frequent twinning; the unusually low value of the lowest refractive index, α, and the extinction relations. The lowest index is matched by methyl salicylate (n = 1.530 to 1.535); and crystals immersed in this liquid disappear in one direction or another with reference to the plane of the polarizer.

SUMMARY

The α- and β-naphthylamine salts of the naphthalene-α-, β-, 1,5-, 1,6-, 2,6- and 2,7-sulfonic acids and the ferrous salt of naphthalene-β-sulfonic acid are described. Their characteristic relative solubilities are shown in Table I and their optical properties in Table II.

TABLE I—RELATIVE SOLUBILITIES OF SUBSTANCES DESCRIBED
(Except the ferrous salt of the β-acid)

NOTE: d. = difficultly soluble; v. d. = very difficultly soluble; sol. = soluble; s. sol. = slightly soluble; mod. = moderately soluble; insol. = insoluble; v. s. = very slightly soluble.

	α-NAPHTHYLAMINE SERIES					
SULFONATE	α	β	1,5	1,6	2,6	2,7
Cold water	d.	d.	v. d.	d.	d.	d.
Hot water	sol.	s. sol.	d.	sol.	mod.	sol.
Cold 95 per cent alcohol	d.	d.	d.	s. sol.	d.	sol.
Hot 95 per cent alcohol	sol.	s. sol.	s. sol.	sol.	s. sol.	sol.
Cold 75 per cent alcohol[1]	sol.	s. sol.	d.	sol.	s. sol.	sol.
Hot 75 per cent alcohol	sol.	s. sol.	d.	sol.	s. sol.	sol.
Cold acetone	insol.	insol.	insol.	insol.	insol.	insol.
Hot acetone	insol.	insol.	insol.	insol.	insol.	insol.
	β-NAPHTHYLAMINE SERIES					
Cold water	d.	v. d.	v. d.	d.	v. d.	d.
Hot water	sol.	mod.	s. sol.	sol.	s. sol.	sol.
Cold 95 per cent alcohol	d.	s. sol.	v. d.	s. sol.	v. d.	d.
Hot 95 per cent alcohol	sol.	mod.	s. sol.	sol.	v. s.	sol.
Cold 75 per cent alcohol[1]	sol.	mod.	d.	sol.	d.	s. sol
Hot 75 per cent alcohol[1]	sol.	sol.	s. sol.	sol.	v. s.	sol.
Cold acetone	insol.	insol.	insol.	insol.	insol.	insol.
Hot acetone	sol.	insol.	insol.	insol.	insol.	insol.

[1] Four volumes of 95 per cent alcohol : 1 volume of water.

TABLE II—OPTICAL PROPERTIES OF SUBSTANCES DESCRIBED

	α-NAPHTHYLAMINE SERIES						FERROUS
SULFONATE	α	β	1,5	1,6	2,6	2,7	β
Habit	plates	needles	plates	rods	grains	rods	plates
Indices:							
α	1.552	1.600	1.600	1.583	1.583	1.560	1.500
β	?	1.650	?	1.730	1.640	1.650	?
γ	1.799	1.725	1.795	1.770	1.690	1.675	1.660
$\gamma - \alpha$	0.243	0.125	0.195	0.187	0.107	0.115	0.160
Usual	α & γ	γ	α & γ	α & γ	means	α	α & γ
Colors	1–2	1	2	2–3	2–3	3	2
Extinction	par.	par.	incl.	17°	incl.	par.	par.
Elongation	indet.	+	indet.	—	indet.	—	indet.
Figure	0	0	rare	occas.	occas.	rare	occas.
2 E	indet.	indet.	indet.	large	large	indet.	large
Sign	indet.	+	indet.	—	—	+	+

	β-NAPHTHYLAMINE SERIES						β-Acid Salt
SULFONATE	α	β	1,5	1,6	2,6	2,7	1,5
Habit	plates	plates	plates	needles	plates	rods	plates
Indices:							
α	1.620	1.640	1.631	1.550	1.610	1.530	1.550
β	1.670	?	1.647	1.700	1.634	1.700	1.700
γ	1.850+	1.730	1.755	1.755	1.830	1.740	1.850+
$\gamma - \alpha$	0.230+	0.090	0.124	0.205	0.220	0.210	0.300+
Usual	α & β	α	α & β	α	α & β	α	α & β
Colors	1–2	1–2	1	3–4	1–2	2–3	3–4
Extinction	par.	indet.	indet.	par.	40°	8°	indet.
Elongation	+	indet.	indet.	—	±	±	indet.
Figure	usual	rare	usual	occas.	usual	usual	occas.
2 E	85°	indet.	75°	large	70°	large	large
Sign	+	indet.	+	—	+	—	+

NAPHTHALENE SULFONIC ACIDS. II—A METHOD FOR THE QUALITATIVE DETECTION OF SOME OF THE NAPHTHALENE SULFONIC ACIDS[1]

By Joseph A. Ambler and Edgar T. Wherry

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During the course of experiments on the sulfonation of naphthalene it became desirable to have a fairly rapid and convenient way of detecting the presence of the various sulfonic acids formed when naphthalene is subjected to the action of sulfuric acid under varying conditions. No readily applicable method is to be

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[1] Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

found in the literature. The identification has always been made by means of the chlorides or amides, which is unsatisfactory for rapid work when dealing with mixtures of two or more of the acids. The technical separations are effected by means of the different solubilities of their calcium or sodium salts, but this method is not adapted to making a qualitative differentiation, for example, of naphthalene-1,6-sulfonic acid from the isomeric 2,7-sulfonic acid, or of naphthalene-β-sulfonic acid from the 2,6-disulfonic acid, since the solubilities of the salts of these pairs of acids are similar.

The use of the salts of these acids with organic bases for qualitative separations was not described by Erdmann and Süvern[1] who studied the solubilities of the aniline, benzidine, and *o*-tolidine salts of the α-, β-, 2,6- and 2,7-sulfonic acids of naphthalene. They state that these salts are very valuable for the isolation of the easily soluble sulfonic acids. Their observation that the aniline salts of the α- and 2,7-acids are soluble in cold water, while the corresponding salts of the β- and 2,6-acids are insoluble, suggested the possibility that salts with other organic bases may have properties suitable for a qualitative distinction of the acids. Accordingly, a large number of such salts were prepared and their properties studied. The most important of these salts have been described in the preceding article, and from an examination of their properties the following method of analysis has been developed. Before attempting this method, the chemist should make and become familiar with the salts described in the preceding article or at least with those which are used in this analytical method. If this is done, he will have very little difficulty in distinguishing the various acids by this method.

ANALYTICAL METHOD

REAGENTS—(1) A freshly prepared solution of ferrous chloride.

(2) A hot saturated solution of α-naphthylamine hydrochloride made fresh just before use by dissolving the free base in hot dilute hydrochloric acid.

(3) A standard normal solution of sodium hydroxide.

(4) A hot saturated solution of β-naphthylamine hydrochloride.

(5) Acetone.

(6) Methyl salicylate (oil of wintergreen or birch).

(7) Microscope fitted with two nicol prisms and a revolving stage.

PREPARATION OF SOLUTION—The sodium salts of the sulfonic acids are prepared free from sulfates by the usual method of treating the sulfonation mass with lime, filtering from calcium sulfate, and treating the calcium salts in solution with sodium carbonate. The solution is then filtered to remove calcium carbonate, and the filtrate is acidified slightly with hydrochloric acid.

The solution may be of any convenient strength. Twenty-five cc. of a 5 per cent solution are in most cases ample for a complete analysis.

QUANTITIES USED—The tests may all be made on small quantities in test tubes; for example, 2 cc. of solution or a few milligrams of solid, unless otherwise stated in the directions. Also, except when removing an acid from the solution, 2 or 3 cc. of the reagent employed are adequate, except as noted below.

TEST FOR NAPHTHALENE-β-SULFONIC ACID

Ferrous chloride added to the cold solution produces a precipitate of glistening micaceous flakes of ferrous naphthalene-β-sulfonate.[1] This may be slow in forming if the amount is small.

If this acid is detected, it is removed from the entire solution by adding a slight excess of ferrous chloride and filtering off the iron salt precipitated. The filtrate is then concentrated to its original volume before making the following test.

TEST FOR NAPHTHALENE-1,5-DISULFONIC ACID

To a portion of the filtrate, heated to boiling, is added an excess of boiling α-naphthylamine hydrochloride solution, and the solution boiled down to its original volume. A granular precipitate of α-naphthylamine naphthalene-1,5-disulfonate,[1] formed while concentrating, indicates the presence of the acid.

Difficulty is sometimes encountered here in causing the insoluble salt to precipitate. If, however, the α-naphthylamine hydrochloride solution is made directly before using, by dissolving the free base in hot dilute hydrochloric acid (decolorizing with norit or bone-black when necessary), and employing a large excess of this reagent, there is no difficulty in obtaining a reaction. The explanation of the fact that a solution freshly prepared from the base is more efficacious than one made, for example, by dissolving the dry hydrochloride of the base in water, or than a solution which has stood for some time, is not known.

In adding this solution, an excess over that required to combine with all the sulfonic acids present must be used, as otherwise the insoluble salt does not form. A possible explanation of this fact may be that the disulfonic acid may form a soluble acid salt with α-naphthylamine.

If 1,5-acid is found, it must be removed from the rest of the solution before making any subsequent tests. To the boiling solution an excess of a boiling solution of the base is added, the mixture is concentrated to its original volume and filtered hot. The excess of the base is then removed from the filtrate by titrating to alkalinity with sodium hydroxide, using phenolphthalein for indicator. After cooling, the free base is removed on a filter, and the filtrate acidified with hydrochloric acid.

TEST FOR NAPHTHALENE-2,6-DISULFONIC ACID

The entire solution which has been freed from both β- and 1,5-acids is heated to boiling, and a large excess of boiling β-naphthylamine hydrochloride solution is added. The amount used must be sufficient to form neutral salts with all sulfonic acids present.

The 2,6-acid is indicated by a white precipitate of β-naphthylamine naphthalene-2,6-disulfonate[2] formed

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[1] *Ann.*, **275** (1893), 297.

[1] See p. 1083 of preceding paper.

[2] See p. 1084 of preceding paper.

while boiling. The solution is filtered rapidly while hot, and the filtrate allowed to cool.

The formation of a crystalline precipitate in the filtrate on cooling does not necessarily indicate the presence of any of the remaining acids, since the β-naphthylamine naphthalene-2,6-disulfonate is not completely insoluble in hot water. However, the presence of other naphthalene sulfonic acids at this point has a salting-out effect on the 2,6-salt, and hence its precipitation is more complete in hot water when some of the naphthalene sulfonic acids are present whose β-naphthylamine salts are soluble in boiling water (the α-, 1,6- or 2,7-acids). When none of these acids are present, the salt separating on cooling is distinctive—white, fine, and voluminous—and when once seen would never be mistaken for the salts of any of the other naphthalene sulfonic acids not yet removed.

TEST FOR NAPHTHALENE-α-SULFONIC ACID

The filtrate from the previous test is allowed to cool and stand at least one hour after it is cold to insure complete crystallization of the difficultly soluble salts. Should a jelly be formed, more water is added, and the solution heated to boiling and cooled again. The salts are then filtered and dried in a vacuum oven at 100° C. The filtrate should be tested with more of the cold reagent to be sure of complete precipitation.

A small quantity of the dry salts is boiled with 2 or 3 cc. of acetone, filtered through a warm, dry funnel, and the filtrate cooled. The presence of α-sulfonic acid is shown in the cold filtrate by the separation of crystals of β-naphthylamine naphthalene-α-sulfonate.[1]

If this acid is found, the whole mass of the salts is boiled with acetone, filtered hot through a warm, dry funnel, boiled again with acetone, filtered, and the residue washed with hot acetone. The insoluble salts are then dried and examined under the microscope.

OPTICAL PROPERTIES—Immerse the salts in methyl salicylate or other oily liquid having a refractive index near 1.53. Turn the stage to bring a clear-cut crystal (rod or plate) into parallelism with the plane of vibration of the polarizing nicol prism (as indicated by one of the cross hairs; which cross hair must be determined in advance).

If the crystal boundaries disappear, indicating the identity of refractive index of the liquid with that of the crystal in the direction of elongation; and if, on inserting the analyzing nicol, in crossed position, the extinction is more or less inclined, *i. e.*, if the crystal becomes dark when turned so as to make an angle of up to nearly 10° with a cross hair, the presence of naphthalene-2,7-disulfonic acid as its β-naphthylamine salt is indicated. This salt of the 2,7-acid also shows a characteristic twinning habit, the two parts of the crystal plates showing extinction in different positions. These twinned plates also show an approximately 120° termination.

If the crystal boundaries remain distinct, and, on raising the microscope tube, a band of light appears to enter the crystal, showing that its refractive index exceeds that of the liquid in the direction of elongation; and if, on inserting the analyzing nicol in crossed position, the extinction is parallel, *i. e.*, the crystal becomes dark when parallel to a cross hair, the presence of naphthalene-1,6-disulfonic acid also as the β-naphthylamine salt is indicated. If salts of both acids are present, both behaviors can be readily recognized on separate crystals.

These optical properties are very characteristic of these two salts, as may be seen by referring to the table of optical properties given in the preceding article. The very small amounts of the salts of any of the other four naphthalene sulfonic acids which may be present at this point of the analysis do not in any way interfere with these observations, and are readily recognized as impurities.

DELICACY OF THE TESTS

Most of the above-described tests are as delicate as it is necessary for them to be when used for technical purposes.

The precipitation of the β- and 2,6-acids is very nearly quantitative, so that a rough estimate of the amounts of these present can be made by weighing the dried precipitates. The precipitation of the 1,5-acid is not so complete, since α-naphthylamine naphthalene-1,5-sulfonate is slightly soluble in boiling water. The α-sulfonic acid salt is almost completely insoluble in cold water, and by evaporating the acetone extract, its weight may be obtained, since none of the other salts are appreciably soluble in acetone. A rough estimate of the relative amounts of the 2,7- and 1,6-salts may be made under the microscope.[1]

SUMMARY

A method is proposed for the qualitative examination of mixtures of the following naphthalene sulfonic acids: α- and β-monosulfonic, and 1,5-, 1,6-, 2,6-, and 2,7-disulfonic acids.

THE MECHANISM OF BATING[2]

By John Arthur Wilson

Laboratories of A. F. Gallun & Sons Co., Milwaukee, Wisconsin

Received August 25, 1920

Perhaps the most curious of all the processes involved in making leather is that of bating. Little is known of its origin because it was a secret process, but it is at least some centuries old. After the skins are taken from the lime liquors, unhaired, and washed, they are plump and rubbery, a condition not particularly suitable for putting them directly into the tan liquors. The object of bating is to prepare the unhaired skins for tanning, and originally consisted in keeping them in a warm infusion of the dung of dogs or fowls until all plumpness had disappeared and the skins had become so soft as to retain the impression of thumb and finger when pinched and sufficiently

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[1] See p. 1082 of preceding paper.

[1] The authors wish to extend their thanks to Messrs. G. O. Oberhelman and D. F. J. Lynch for their kindness in checking and confirming this method, and for suggestions they have made for its improvement.

[2] Presented before the Section of Leather Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., Sept. 6 to 10, 1920.

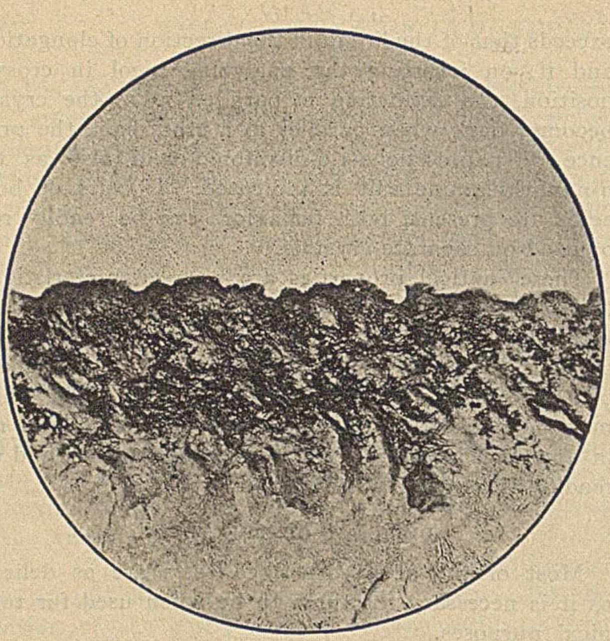

Fig. 1—Cross Section of Grain and Papillary Layer of Calfskin Bated without Trypsin. Note Elastin Fibers in Upper Half. Magnification 42 ×

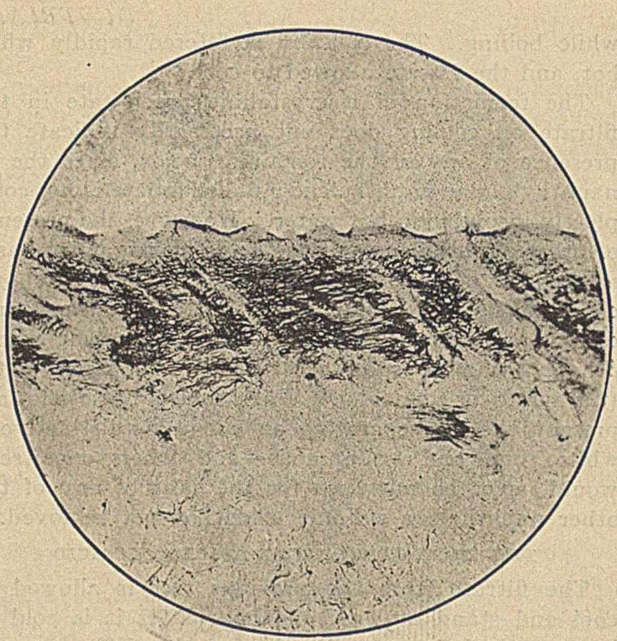

Fig. 2—Cross Section of Grain and Papillary Layer of Calfskin Bated for 6 Hrs. with Trypsin. Elastin Fibers Partly Removed. Magnification 42 ×

porous to permit the passage of air under slight pressure. In his book Wood[1] says:

> The object of bating or puering is to render the skins, and the resulting leather, soft and supple. * * * Puering is not only a filthy and disgusting operation, but is prejudicial to health and in the nature of it is attended by more worry and trouble than all the rest of the processes in leather making put together.

Wood made a thorough study of dungs and their action upon skins and his final opinion was that the active constituents of the dung infusions were ammonium compounds and pancreatic or similar enzymes. As a result of this work, and some practical development by others, dung has been replaced as a bating material in many tanneries by a mixture of ammonium chloride and pancreatin.

Our knowledge of the behavior of proteins in contact with aqueous solutions of acids, bases, and salts, in which the protein swells by absorption of water to an extent depending upon the nature and concentration of the electrolyte, raises the question as to whether bating is not simply a means of bringing the skins into a condition of minimum swelling, especially since such a condition would give the skins those physical properties which are widely accepted as indicative of properly bated skins. If this were so it would reduce bating to perhaps the simplest of the tannery processes.

EXPERIMENTAL

The following experiment was made to show the comparative degrees of swelling of hide in lime water, in a bate liquor, and in water. In each of three 100 cc. graduated cylinders were placed 2 g. of "Standard" hide powder. The first was filled with saturated lime water, the second with distilled water, and the third with a bate liquor showing a value for log H^+ of —8.1. The cylinders were stoppered and shaken at intervals, and the swollen powders allowed to settle. At the end of 8 hrs. the volumes occupied by the powders were as follows: in lime water 41 cc., in distilled water 32 cc., and in the bate liquor 31 cc., showing that the bate liquor actually causes less swelling of hide than ordinary distilled water. A pure solution of ammonium chloride of the same concentration and alkalinity as the bate liquor produces practically the same degree of swelling.

A more practical test was made by comparing the action of ammonium chloride alone with that of a commercial bate, supposedly containing ammonium chloride and pancreatin. Both liquors were made up to a concentration of 1.20 g. of ammonium chloride per liter, skins of similar nature were put into each, and all other conditions kept as nearly alike as possible. At the end of several hours the skins in both liquors had all the physical properties of bated skins and no difference between the two lots could be detected, even after tanning. Recently a number of chemists in various parts of the country have informed the author of similar findings. This test would seem to indicate one of two things—either that pancreatin was of no practical benefit, or else that the commercial bate was deficient in enzymes.

Some years ago Rosenthal[2] concluded that the bating process removes elastin from the skin. In a sample from the butt of a calfskin he found 10.36 per cent of elastin, calculated on the dry basis, before bating, and only 0.31 per cent after bating. But, as a measure of the elastin content of a skin, he used the per cent of nitrogenous matter that could be rendered soluble by tryptic digestion, whereas his bating process was also supposedly a tryptic digestion. What he proved was merely that bating removed almost to completion certain nitrogenous matter from the limed skin, but whether this was elastin or hide substance

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[1] "Puering, Bating and Drenching of Skins," Spon, **1912**.

[2] *J. Am. Leather Chem. Assoc.*, **11** (1916), 463.

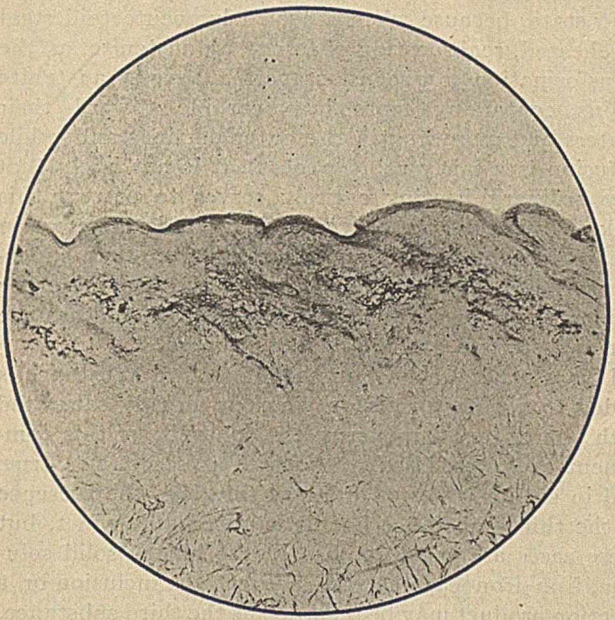

FIG. 3—CROSS SECTION OF GRAIN AND PAPILLARY LAYER OF CALFSKIN BATED FOR 20 HRS. WITH TRYPSIN. FEW ELASTIN FIBERS LEFT. MAGNIFICATION 42 ×

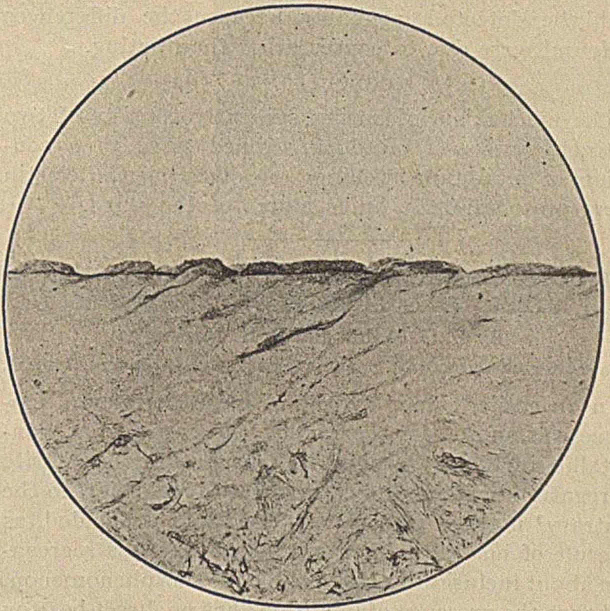

FIG. 4—CROSS SECTION OF GRAIN AND PAPILLARY LAYER OF CALFSKIN BATED FOR 24 HRS. WITH TRYPSIN. ELASTIN FIBERS ENTIRELY REMOVED. MAGNIFICATION 42 ×

which had previously been attacked by lime appears open to question.

The statement that elastin is removed by bating is also made by Moeller[1] and by Seymour-Jones,[2] who in collaboration with Wood carried out an interesting experiment on the bating of sheepskin. The "flywing" grain of a sheepskin was split from the main body of the skin, called simply flesh for convenience, and both grain and flesh were cut into halves along the backbone. One grain and one flesh were bated with pancreatin, while the other halves were delimed with acetic acid, but not bated. All four pieces were then tanned with sumac. There was comparatively little difference between the bated and unbated flesh halves, but the grain samples were very different from each other. The bated grain was soft and even, with the hair-holes clean and clear, but in the unbated grain the hair-holes appeared to be glued up and the surface had a rough, contracted appearance. Seymour-Jones concluded that elastin is present only in the grain membrane and that it must be digested before tanning to produce a satisfactory grain, but that bating of the skin under the grain is not only unnecessary, but often undesirable.

The results of this experiment may, however, not have been due to the bating process. since one grain had been treated with acetic acid, while the other apparently had not. The author recalls having tanned in the same liquor a bated skin and one both bated and pickled. The difference between the tanned skins was striking, the pickled skin being shriveled to half of its original area and having an almost corrugated appearance, while the other had not shrunk at all and was quite smooth.

It was decided to settle definitely the question of the removal of elastin in the bating process by means of photomicrographs of cross sections of the skins taken before and after bating. The elastin fibers are not clearly discernible unless suitably stained, and for this purpose magenta has been found excellent, since it makes the elastin much darker in color, and therefore more prominent than the rest of the skin. Two liquors were prepared, each containing 1.20 g. per liter of ammonium chloride, while one also contained 0.03 g. per liter of a U. S. P. grade of trypsin. Enough alkali was added to each to make the value for log H^+ about —8.0. A piece of limed calfskin was kept in each of these liquors for 24 hrs. at about 37°. Microscopic examination of the sample from the trypsin liquor showed that practically all of the elastin had been removed, while, in the piece treated with ammonium chloride only, the elastin was left apparently unaltered. The test was carried out on a large scale with the same result.

The time factor in the removal of elastin can be followed by means of the photomicrographs shown in Figs. 1 to 4, inclusive.[1] The sections, which are all 40μ thick, have been stained with magenta to make the elastin fibers more prominent. In Fig. 4 the grain membrane shows clearly enough to be measured, and is about 0.046 mm. thick. The skins are from medium-size calves, and all sections shown were taken from the butt. In a section 2.5 mm. thick the elastin fibers were present to a depth of 0.5 mm. from the grain surface, then for a distance of 1.7 mm. no elastin could be detected, but was abundant in the remaining 0.3 mm. of flesh surface. This fully confirms the view of Seymour-Jones that the main body of skin contains no elastin.

The value of removing elastin from skins must depend to some extent upon the particular properties desired in the leather, but between skins containing elastin and those from which it had been removed no such differences as were noted by Seymour-Jones

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[1] *Collegium*, **1918**, 105, 125; *Chem. Abs.*, **12** (1918), 2706.

[2] *J. Soc. Leather Trades' Chem.*, **4** (1920), 60.

[1] Acknowledgment is made of the assistance of Mr. Guido Daub in the preparation of the photomicrographs.

could be detected, probably because the differences he found were due to causes other than bating.

CONCLUSION

The mechanism of bating evidently consists of two distinct parts: (1) Reducing limed skins to a condition of minimum swelling; (2) digesting the elastin fibers present in the outer layers of the skins.

INCLUSIONS AND FERRITE CRYSTALLIZATION IN STEEL. II—SOLUBILITY OF INCLUSIONS[1]

By E. G. Mahin and E. H. Hartwig

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In an earlier paper by one of us[2] experimental evidence was offered for the widely held theory that nonmetallic inclusions are partly responsible for ferrite segregation in steel, indicating that Stead's view to the contrary[3] may be incorrect. Stead had concluded, as a result of his experiments, that phosphorus segregation about inclusions is responsible for this phenomenon, and that the presence of inclusions has no direct bearing upon ferrite formation from slowly cooled hypoeutectoid steels. The writer, on the other hand, showed that ferrite continues to segregate about inclusions even after long heating at temperatures considerably above Ar_3, although the longitudinal ferrite streaks of rolled steel disappear because of the better dissemination of phosphorus that is brought about by such heating.

To account for this definitely established fact, it was assumed that either the material of the inclusion itself or some reaction product of this with surrounding metal (or both of these) is soluble, to a slight extent at least, in iron or in austenite, and that the presence of this dissolved material so alters solubility relations as to cause the beginning of ferrite separation from austenite in the regions so penetrated, before supersaturation has broken down at other points.

The mechanism of the breakdown of the solid solution of hypoeutectoid steel is somewhat as follows:

As the steel cools slowly through the transformation range, the austenite of higher temperatures becomes saturated with ferrite at the ideal temperature, A_3. Ferrite does not, in any case, separate at this point, but remains in solution until a somewhat lower temperature, Ar_3, is reached, when the supersaturation then existing can no longer be maintained. When ferrite separation begins, recalescence occurs, and austenite continues to reject ferrite about the crystal nuclei thus formed until the temperature has fallen to Ar_1, when austenite of eutectoid composition remains and is changed bodily to pearlite.

However, it is not to be supposed that the *degree* of supersaturation of ferrite in austenite is the same in all parts of the steel mass, or even in all parts of a given austenite grain. Austenite of absolutely uniform concentration is an ideal substance, probably never existing in a given steel mass. Even if all elements but carbon and iron could be excluded, such uniformity could be approached only in steel cooling from the liquid state, because when a cooled hypoeutectoid steel is reheated, reabsorption of ferrite by austenite, as the transformation range is traversed, gives austenite grains containing more iron carbide toward their centers and more iron in the outer portions and, while diffusion is a fairly rapid process, it is not likely that any ordinary heating entirely serves to correct this lack of uniformity in concentration. It is therefore in the regions of higher iron concentration that supersaturation during cooling is greatest and, leaving other influences out of account, it is in these regions that the nuclei of ferrite grains are first generated.

It is a general condition that if a third substance is added to a binary solution which is already saturated with one of its components, the solubility of this component is lowered. The opposite is sometimes true, and in certain cases of ordinary solutions the presence of the third substance has little observable effect, but these cases are exceptional. In the binary solid solution, iron–iron carbide, the nonmetallic inclusion or a reaction product may be regarded as the third substance. It is not necessary to assume a large solubility for this third substance. If there is a zone, however narrow, lying about an inclusion and containing even a trace of some third dissolved substance derived from the inclusion itself, the presence of this material should alter the solubility of ferrite in the austenite there present, and thus cause local breakdown of the cooling solution first in these regions. This would establish ferrite nuclei, and separation would continue at these points. The cooled steel would then show inclusions embedded in ferrite.

One reaction product was suggested in the first paper. This was manganese, an equilibrium product resulting from contact of manganese sulfide inclusions with iron. It would appear that the steel in contact with such an inclusion must necessarily contain manganese in slightly higher concentration than in other regions. This would also be true of manganese sulfide itself and of ferrous sulfide existing in equilibrium with the other substances involved in the reaction.

Similar reactions are conceivable in the case of oxides, silicates, sulfides, etc., of elements other than iron, and the reaction products, as well as the original inclusions, must dissolve to a slight extent in the surrounding metal.

It was earlier pointed out that the effort to produce artificial inclusions by sealing powders into holes in steel could not be expected to produce any very definite results, because air could not be entirely excluded from such cavities, and the film of oxide produced on the lining of the cavity when the steel was heated must prevent intimate contact with the inclusion, even if the latter were fusible. Of nine materials used by Dr. Stead, at least five (calcium fluoride, calcium oxide, magnesium oxide, silica, and manganese sulfide) would be infusible, or practically so, at 1000° C., the temperature employed.

The difficulties attending the production of intimate contact of artificial nonmetallic inclusions with surrounding metal are not encountered if metallic inclusions are used. Clean holes may be drilled in the steel, and clean, tightly fitting rods of a different material

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[1] Read at the 59th Meeting of the American Chemical Society St. Louis, Mo., April 12 to 16, 1920.

[2] Mahin, This Journal, **11** (1919), 739.

[3] *J. Iron and Steel Inst.*, **97** (1918), 287, 389.

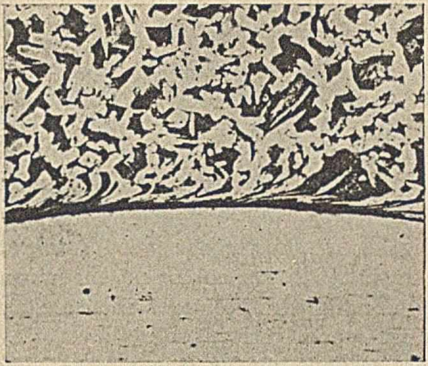

Fig. 1—Aluminium Bronze (Below) in Steel. Not Heat Treated. × 100

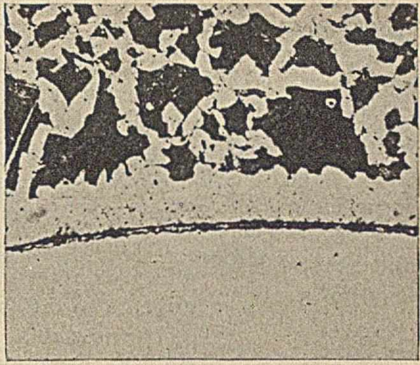

Fig. 2—Aluminium Bronze in Steel. Heat Treated. × 100

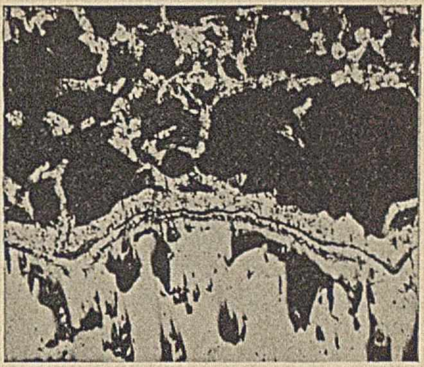

Fig. 3—Zinc-Aluminium Alloy in Steel. × 100

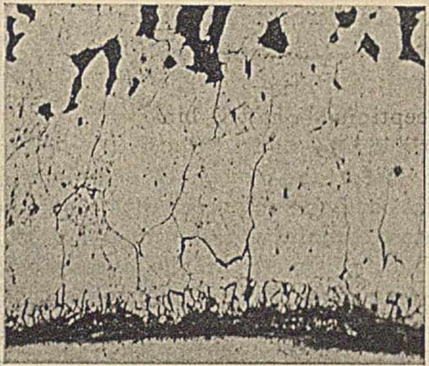

Fig. 4—Stellite in Steel. × 100

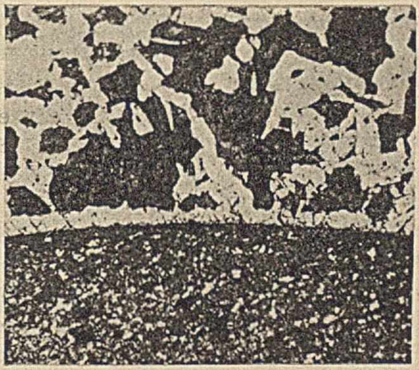

Fig. 5—High-Speed Steel in Carbon Steel. × 100

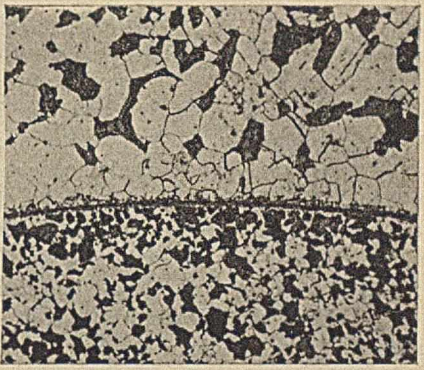

Fig. 6—Steel (Mn 1.74%) in Steel (Mn 0.67%). × 100

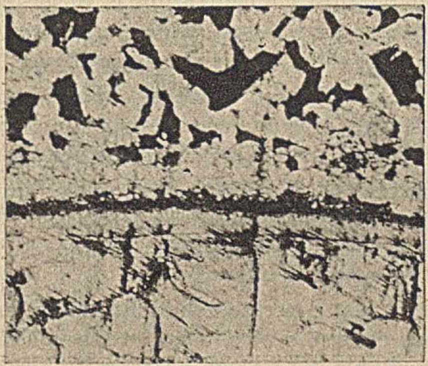

Fig. 7—Illium in Carbon Steel. × 100

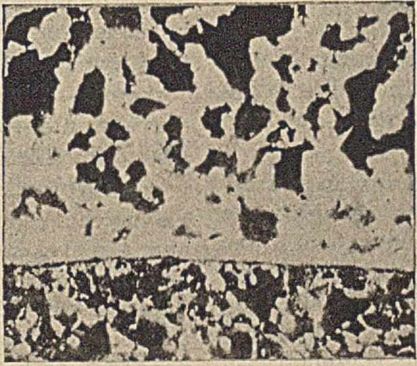

Fig. 8—Steel (Cr 1.0%) in Carbon Steel. × 100

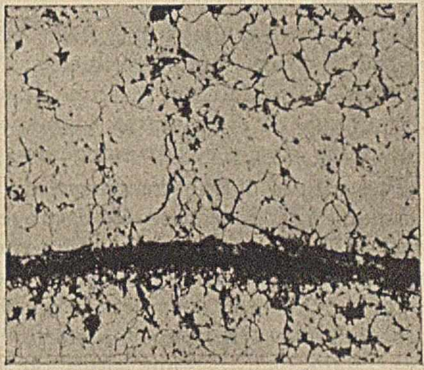

Fig. 9—Steel (Ni 3.5%) in Carbon Steel. × 100

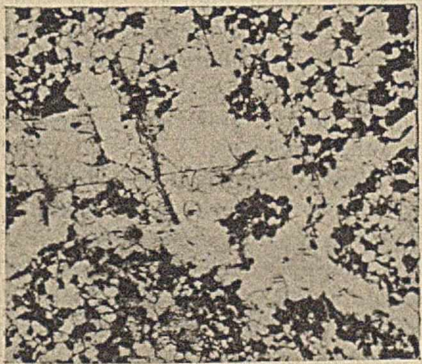

Fig. 10—Titanium Steel with Segregated Ferrite. × 100

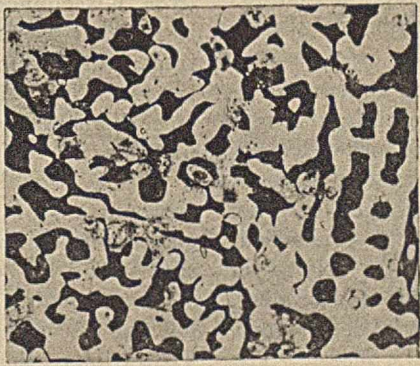

Fig. 11—Steel (Si 4.0%). × 50

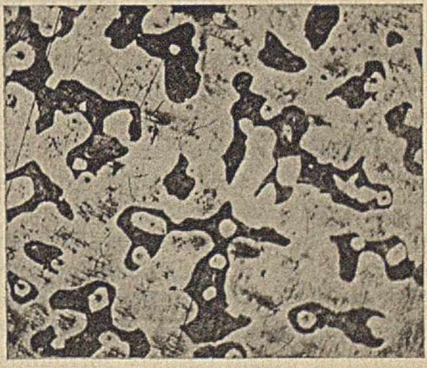

Fig. 12—Steel (P 1.06%). × 50

driven into the cold, unoxidized steel. In this way it is possible to use nonferrous metals, alloys, or alloy steels to determine the effect of a third metal or combination of metals, thus imitating the production of a metal by reaction of a nonmetallic inclusion with surrounding steel. This was the idea which prompted the work described below. From the success attained the work was extended to include an investigation of the broader question as to the effect of segregation of such substances as silicides, sulfides, and phosphides, and of metallic elements of alloy steels, upon carbon distribution.

EXPERIMENTAL PART

A bar of rolled carbon steel, containing 0.53 per cent carbon, was cut transversely into plates about one inch in thickness. Through these were drilled holes one-eighth inch in diameter, no oil or cutting compound being used. Rods of a number of alloys, carefully turned to 0.002 in. oversize, were driven into these holes. The ends of such as were sufficiently malleable were riveted down. The piece of steel, with its insert, was then placed in a closed muffle furnace and heated to 850° C. (which was well above the transformation range for this steel) for periods of 7 hrs. After cooling in the furnace the pieces were sectioned transversely to the axis of the insert, polished, and etched in nitric acid. Microscopic examination of the polished sections was made before etching, to determine whether contact of the pieces had been perfect. In the few cases where the insert had not been fitted tightly the specimens were rejected. Of the others, photomicrographs were made for record.

The following alloys and steels were used as inserts in the first series of experiments: Aluminium bronze (copper 90, aluminium 7, iron 3), stellite, die-casting alloy (zinc and aluminium), high-speed steel, and steel containing 1.74 per cent manganese.

The results of the treatment are shown in the accompanying photomicrographs, in each of which the steel and the insert are shown in the upper and lower portions, respectively. A well-defined ferrite ring surrounding the insert is evident in all cases. (In all of the photomicrographs there is a narrow, dark line, somewhat indistinct in some cases, at the contact circle separating steel and insert. This is due to the fact that there is usually a difference in hardness of the steel and insert, so that polishing produces a rounded shoulder at the contact surface. With vertical illumination this appears as a dark ring.)

ALUMINIUM BRONZE—Fig. 1 shows the appearance of the contact line between steel and aluminium bronze insert before thermal treatment. The other experimental pieces were similar to this in appearance. The contact is excellent, the only change in grain structure being a physical distortion of grains adjoining the insert, this being produced by driving in the cold insert. Fig. 2 shows the same piece after 7 hrs. heating at 850° C. A ferrite ring, clearly defined and uniform in width, entirely surrounds the insert. The obvious assumption is that outward diffusion of the foreign metal, dissolving in contiguous austenite, lowers ferrite solubility and causes separation first in the zone penetrated.

ZINC-ALUMINIUM—The die-casting alloy was heated above its fusing point, and the line representing the contact surface of the cavity and melted metal has become irregular. However, the ferrite ring, not so wide in this case, follows this outline, as shown in Fig. 3.

STELLITE—In Fig. 4 is shown the very striking effect of a stellite insert. Either cobalt or chromium appears to diffuse quite rapidly into steel and to exert a considerable effect upon ferrite solubility. Possibly both metals are responsible for this effect. The ferrite ring here produced is the widest of all that were obtained in the experiments described in this paper, with the exception of that produced by manganese and nickel, to be discussed later.

CHROMIUM-TUNGSTEN—The action of a high-speed steel insert is illustrated in Fig. 5. The ferrite ring is narrow, but regular in width, and very distinct.

MANGANESE—The action shown in Fig. 6 is interesting. Here the insert and the steel body are of practically identical composition except with regard to manganese, the insert containing 1.74 per cent of this element as against 0.67 per cent in the outer body. Above the transformation range, manganese has diffused outward from the region of greater concentration into that of lower concentration. Ferrite solubility has apparently been diminished in the outer piece and, as might have been predicted, somewhat increased in the outer border of the insert. Consequently, a ring of increased pearlite concentration is observed in the last-mentioned zone. (A still wider ferrite ring, produced by manganese diffusion, is shown in Fig. 17.)

ILLIUM—Illium metal (chromium-nickel-copper) produces a narrow ferrite ring when the specimen is heated for 9 hrs. at 850° C. This is shown in Fig. 7.

CHROMIUM AND NICKEL—A chrome steel (chromium 1.0 per cent) shows a well-characterized effect (Fig. 8), and a nickel steel (nickel 3.5 per cent) produces a wide ferrite band, as shown in Fig. 9.

In the experiments just described the materials used as pseudo-inclusions consisted of alloys and steels that happened to be available, and they were used in this way to test the general effect of localizing metallic impurities. In the further attempt to use inserts made from miscellaneous steels, each high in some single element, it was soon found that the results of the heat treatment were complicated by differences existing between the insert and body, with respect to the per cents of carbon, as well as of the common elements, silicon, phosphorus, sulfur, and manganese.

The National Malleable Castings Co., through the courtesy of Mr. H. A. Schwartz, chief metallurgist, kindly undertook to prepare a set of special steels that would be better adapted to this use. One stock steel was made, containing 0.5 per cent of carbon and normal per cents of the four other common elements. To various other portions of this same steel abnormally high amounts of special elements were added in the crucible. These special steels were used as in-

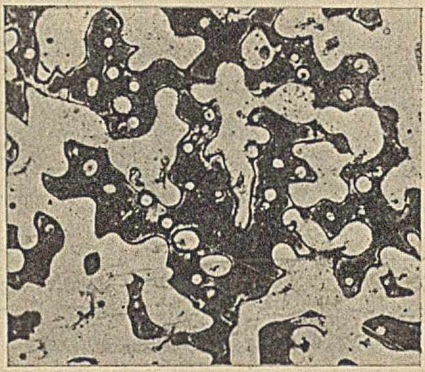

FIG. 13—SAME STEEL AS IN FIG. 12. COPPER REAGENT. × 50

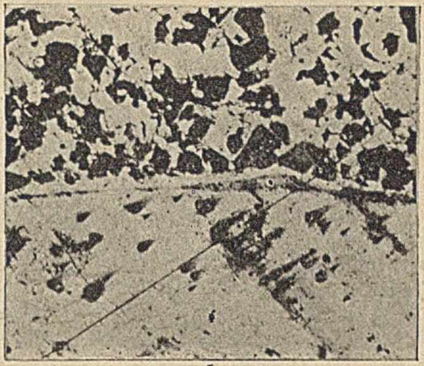

FIG. 14—SAME STEEL (BELOW) AS IN FIG. 12 IN CARBON STEEL. × 100

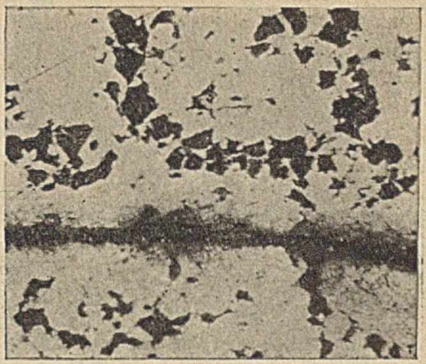

FIG. 15—STEEL (S 1.36%) IN CARBON STEEL. × 100

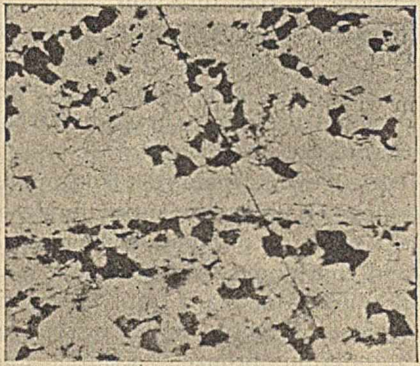

FIG. 16—STEEL (CU 1.34%) IN CARBON STEEL. × 100

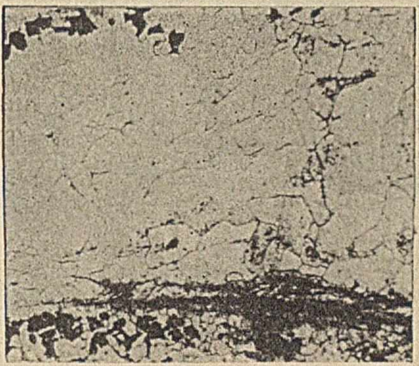

FIG. 17—STEEL (MN 1.46%) IN CARBON STEEL. × 100

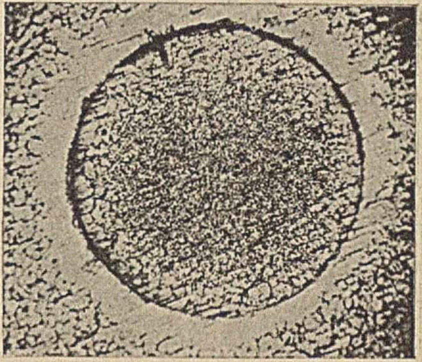

FIG. 18—SAME AS IN FIG. 17. × 12

serts in the stock for heat treatments similar to those described in the first part of this paper. The following per cents of the special elements were found by analysis: Phosphorus 1.06, sulfur 1.36, silicon 4.0, manganese 1.46, chromium 0.84, and copper 1.34. A special titanium steel also was available, but the experiments upon this are still incomplete. Some further work upon all of these specimens is still in progress, but it may be of interest to dwell briefly upon the effects of some of the special elements upon carbon distribution.

The method used for making the special steels was, as noted above, the addition of ferromanganese, ferrosilicon, and ferrotitanium, as well as of steels containing high proportions of iron phosphide, iron sulfide or chromium, to a crucible containing fused carbon steel. The carbon was thus maintained practically constant, but under the conditions it could scarcely be expected that the special steels would be uniform in composition, with respect to the special element added. This lack of uniformity in the special steel insert gives two interesting results:

(1) The ferrite ring produced in the carbon steel surrounding the insert varies greatly in width, presumably according to the variation in concentration of the special element along the cylindrical surface of the insert.

(2) The special steel itself shows pronounced carbon segregation.

The latter point is illustrated by Figs. 10, 11, and 12, photomicrographs of the annealed titanium, silicon and phosphorus steels, respectively. The segregated masses of ferrite grains probably contain a higher proportion of the special element than other parts of the metal. This is proved to be the case, at least with the phosphorus steel, by a comparison of Figs. 12 and 13, the latter being a representation of this special steel attacked by Stead's copper reagent. The bright high-phosphorus areas, free from copper, correspond well with the ferrite grains of Fig. 12.

PHOSPHORUS—It has already been noted by Stead, and confirmed by the work reported in a previous paper by one of the present writers,[1] that iron phosphide migrates very slowly in austenite. It is interesting to notice that the insert of steel containing 1.06 per cent of phosphorus, when heated to 850° C. for 4 hrs., produces only a very narrow (and somewhat irregular) ferrite ring in the steel surrounding the insert (Fig. 14). It is planned to give this specimen a protracted heat treatment at a higher temperature in order to observe whether the effect will be more pronounced.

SULFUR—The effect of sulfur, through migration of ferrous sulfide, is shown in Fig. 15. The contact line is somewhat obscured, in this view, on account of the smearing that occurs during the polishing action upon the somewhat brittle material.

COPPER—Copper migrates readily and affects carbon distribution, as do the other elements noted (see Fig. 16).

MANGANESE—Manganese shows a more pronounced effect than does any other of the common elements

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[1] *Loc. cit.*

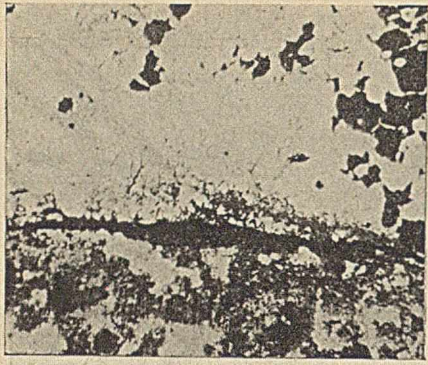

FIG. 19—STEEL (SI 4.0%) IN CARBON STEEL. × 100

FIG. 20—BRASS IN CARBON STEEL. AIR POCKET. × 100

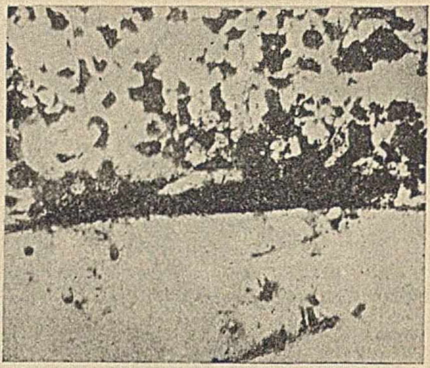

FIG. 21—STEEL (P 1.06%) IN CARBON STEEL. AIR POCKET. × 100

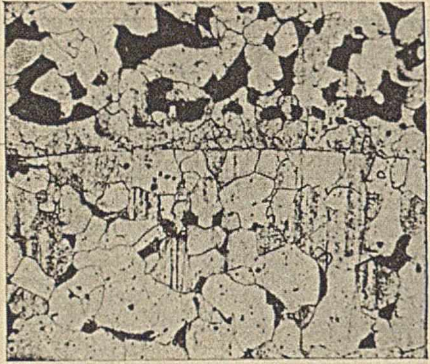

FIG. 22—INGOT IRON IN CARBON STEEL, SHOWING CARBON PENETRATION. × 100

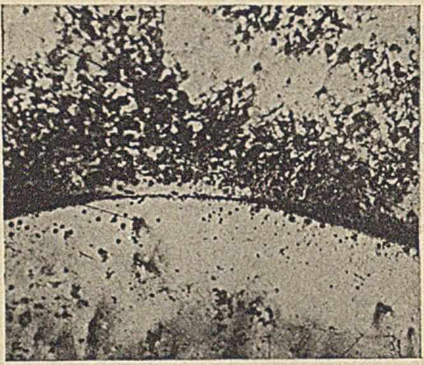

FIG. 23—STEEL (P 1.06%) IN CARBON STEEL. TWO AIR POCKETS SEPARATED BY LINE OF GOOD CONTACT. COPPER REAGENT. × 50

of ordinary steel. Figs. 17 and 18, at 100 and 12 diameters, respectively, illustrate this very marked effect. A wide ferrite ring, uniform in width, is shown in both figures. Fig. 18 was made without using the ocular of the microscope and the definition is not good, but the etching effect is easily seen.

SILICON—In Fig. 19 the effect of silicon is shown. The ferrite patches about the insert are very wide in places, and very irregular. The irregularity is, no doubt, due to lack of uniformity in distribution of iron silicide in the special steel.

OXIDATION

Throughout this discussion it has been assumed that diffusion of the special element or compound from the insert into the adjacent steel has been the cause of ferrite segregation near the contact surface. It is worth while to inquire whether oxidation may have had some influence, through leakage of air into minute cavities caused by badly fitting inserts, with resulting oxidation of carbon. Five lines of evidence lie against this possibility:

1—Microscopic examination of the polished section easily discloses points of poor contact, and ferrite segregation is almost invariably most marked where contact is closest.

2—Oxidation should act upon steel insert and body alike. If the inner lining of the hole in the body is to be decarburized by oxidation, the outer layers of the insert also should be decarburized, where the insert is of steel. Figs. 5, 6, 8, 9, 16, 17, and 18 very strikingly dispose of this question. Fig. 14 gives no evidence on this point, because the etching that is appropriate for the plain carbon steel does not bring out the grain structure of the phosphorus steel.

3—It would require a continuous inflow of air to the entire lining of the cavity to produce such a regular and continuous ferrite band as was produced in many of the experiments, notably with inserts of aluminium bronze, stellite, and manganese steel, where the contact was exceptionally good.

4—The actual amount of carbon that could be oxidized by the minute amount of air enclosed in an occasional cavity, caused by using a poorly fitting insert, is necessarily small, and migration of iron carbide would quickly replace that destroyed by oxidation. Fig. 20 shows a pronounced air pocket between a plain carbon steel and a brass insert, while Fig. 21 illustrates a similar condition with the special phosphorus steel insert already discussed. In both cases any carbon that has been removed by oxidation has been replaced by carbide migration, so that pearlite grains extend to the very border of the cavity.

This ability of iron carbide to migrate readily is, of course, well known, and it is the basis for such commercial processes as case carburizing. That iron carbide can easily and continuously cross the border joining these metallic inserts with surrounding steel is, finally, illustrated by using an insert of Armco ingot iron. After giving this specimen the same treatment as was given the others, pearlite was found over the entire cross section of the insert. This is shown in Fig. 22. This is sufficient proof of perfect metallic contact.

5—Actual diffusion of iron phosphide from the special phosphorus steel is shown by use of Stead's copper reagent. Fig. 23 is from a photomicrograph taken to include two regions where there was no contact, separated by a short line of good contact. It is only into the region immediately outside the contact surface that phosphide has migrated, as is shown by the absence of a copper deposit. It may be noted also that the bright surface here shown is of approximately the same width as the ferrite ring shown for this same specimen in Fig. 14.

In addition to the experiments above described, a few metals and alloys used as inserts in heat-treated steels have failed to give any striking results. Whether this has been due to (*a*) failure to heat to the necessary temperature, (*b*) extremely low migration velocities of the special elements or compounds, or (*c*) absence of any effect of diffused material, is not now clear. These materials and others will be used for additional experiments.

SUMMARY

A considerable number of alloys and special steels have been turned into small rods and driven into holes in carbon steels, the whole assembled specimen then being heated to temperatures above the transformation range for the steel. The section of the slowly cooled piece then shows, in nearly all cases, ferrite segregation around the insert. The hypothesis that has been advanced to explain this phenomenon is to the effect that the special element, elements, or compounds have diffused into the surrounding steel, and that they have there exerted an influence toward throwing ferrite out of the austenitic solution when the latter cools into the transformation range.

These experiments are cited as possibly throwing some light upon the character of the influence of nonmetallic inclusions upon ferrite segregation. The inclusion must have a certain slight solubility in austenite, and the concentration of the dissolved matter is therefore greatest in the immediate vicinity of the inclusion. There must also be equilibrium products of reactions occurring between the material of the inclusion and the steel. These products also must have a slight solubility, and they also are localized about the inclusion. Such a condition of localized dissolved impurities might have the effect of starting ferrite crystallization first about the inclusion, thus breaking down the state of ferrite supersaturation that always occurs in hypoeutectoid steels between the temperatures A_3 and Ar_3.

If these hypotheses are correct it is easy to see the importance of uniform distribution of all elements of carbon steel, as well as of alloy steels, as otherwise it is not possible to have uniform carbon distribution, and the finished piece cannot be brought into its best condition by any ordinary heat treatment.

The effect of phosphorus upon carbon distribution is then but one illustration of the general law. Practically all of the elements that can enter steel can exert a similar influence. The importance of this fact in connection with the subject of nonmetallic inclusions comes from the fact that the inclusion furnishes a continuous supply of the dissolved impurity, and that therefore no amount of heat treatment can cure its evil effects, while the opposite is true with the dissolved element or compound that is not associated with discrete particles of inclusions.

AN ELECTROMETRIC METHOD FOR DETECTING SEGREGATION OF DISSOLVED IMPURITIES IN STEEL[1]

By E. G. Mahin and R. E. Brewer

Department of Chemistry, Purdue University, Lafayette, Indiana

Received July 23, 1920

As a result of work described in two earlier papers[2] it was concluded that segregation of dissolved material derived from nonmetallic inclusions, as well as dissolved phosphides, silicides, sulfides, and elements of alloy steels, causes carbon segregation in steel, iron carbide usually leaving the region of higher concentration of impurity as the steel cools from above Ar_3.

In such a case the ferrite grains of the regions so contaminated should possess a solution tension different from that of purer grains in other parts of the steel body. An electrolytic cell in which two of such grains form the electrodes against a common electrolyte, as for example

impure ferrite–KCl–pure ferrite,

should generate an electromotive force which could be measured by use of a suitable potentiometer system.

It is manifestly impossible to isolate two ferrite grains of a given piece of steel in such a way as to make an e. m. f. measurement of such a cell practicable. On the other hand, it should be possible, at least in principle, to make successive measurements of the e. m. f. of each of two systems, in each of which a standard calomel or hydrogen electrode is connected against the grain in question, the same electrolyte being used in the two cases. In this way a comparison could be made of the electrode potentials of various grains of apparently pure ferrite and differences in degree of purity detected.

PRECAUTIONS TO BE OBSERVED

Many precautions must be observed in the attempt to apply this method in practice. Some of these may be enumerated briefly as follows:

1—Immersion of the specimen in the electrolyte is, obviously, not practicable. It then becomes necessary to pick out certain areas in the polished and etched section, making contact of the electrolyte with these alone. The microscope must be used for observation of the specimen, and an extremely fine point of some sort must be used for touching the grain under investigation, this point carrying the solution of the electrolyte and establishing the necessary connection with the remainder of the circuit.

2—In any electrode-potential measurement, contact of electrode with electrolyte must be maintained for a certain period of time, in order to establish equilibrium conditions. Using the method here discussed, it then becomes necessary to maintain a microscopic point or tube in contact with the grain under observation for some time. This presents considerable mechanical difficulties.

3—Evaporation of water from the solution at the point changes the concentration of the electrolyte at the contact surface. Using a molar solution of potassium chloride, the relative change in concentration is

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[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] This Journal, **11** (1919), 739; **12** (1920), 1090.

not serious except in case measurements of a high degree of precision are desired.

4—The positive component of the double layer over the electrode contains ferrous ions, but oxidation of these ions occurs to some extent during the time that is required for equilibrium to be established. To prevent this a current of hydrogen was directed over the specimen during the earlier experiments. It was soon found that this made little observable difference in the values obtained and its use was discontinued.

5—Polishing produces a layer of amorphous metal over the crystalline structure underneath, according to the now generally accepted theory of Beilby.[1] This amorphous (strained) material is slightly more positive than crystals of the same material.[2] This layer is removed by etching, so that it should have no effect upon experimentally determined values.

6—Etching the specimen with nitric acid in alcohol might, conceivably, produce a condition of slight passivity of the iron. This was tested by comparing the potential of such a specimen with that of the same specimen etched with alcoholic hydrochloric acid, a less satisfactory etching solution from the standpoint of clearness of the etched surface. There was no consistent difference between the two sets of values.

7—Exposure of the surface to the air before testing gradually raises the electrode potential by oxidation. This interference was avoided by polishing and etching each specimen just before making the measurements.

Greater precautions with regard to all of these points would have to be taken if a high degree of precision were required. But even in the purest steel there will be so much variation in either ferrite or pearlite grains, from point to point, that values will probably have little significance beyond the third, or possibly even the second, decimal place.

EXPERIMENTAL

APPARATUS—Fig. 1 illustrates the manner of assembling the apparatus, the illuminating system and potentiometer being omitted from the drawing. The specimen under investigation had a short copper wire soldered to its lower surface, this wire dipping into a cup of mercury placed beneath the stage of the microscope. This made a connection with the potentiometer which permitted focusing the stage of the metallographic microscope at will. The specimen was held by a Sauveur magnetic holder. This, of course, resulted in grounding the specimen through the microscope. Experiments carried out with the specimen insulated from the microscope and with a nonmagnetic holder showed that neither of these factors affected the observations of the e. m. f. in the third decimal.

The electrolyte was a molar solution of potassium chloride in boiled distilled water. A solution of ferrous sulfate is not suitable for this purpose because of the facility with which hydrolysis and oxidation take place. A clear solution cannot be kept without having an excess of acid present.

Contact with the specimen was made by means of a very fine, capillary, glass tube, G, drawn to hair-like dimensions. An attempt was first made to use a porous or tubular fiber, either animal or vegetable, cemented in the end of a fine tube. No success has as yet been attained in this direction. Further experiments along this line are in progress. Fig. 2 will indicate the appearance of the capillary point as applied to one of the ferrite rings obtained in the course of the work described in the second paper dealing with this subject.[1] It will be noticed that only the tip of the tube is in focus, so that the grain structure of the steel is visible through the upper part of the tube.

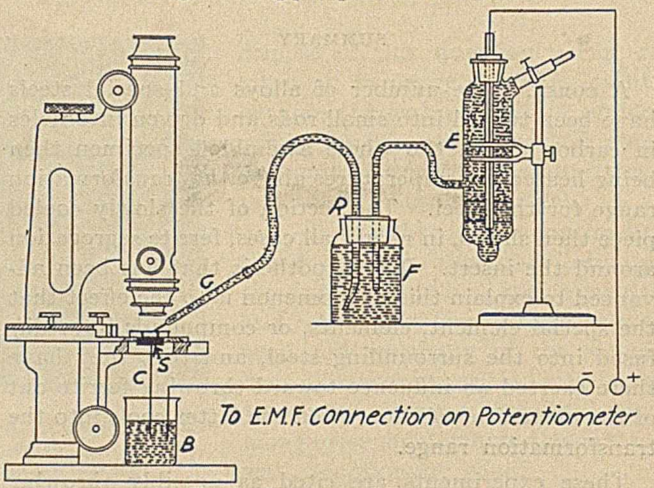

FIG. 1—ASSEMBLED APPARATUS
B—mercury; C—copper wire; S—specimen of steel; G—glass tubing with capillary point; R—rubber tubing; F—molar KCl; E—normal calomel electrode

A normal calomel half-element completed the electromotive system, and a Leeds and Northrup precision potentiometer, with wall-type galvanometer having a sensitivity of 93 megohms, was used for making the measurements by the Poggendorff compensation method. The apparatus was shielded from the interference of stray fields by the method of White.[2]

For the illumination of the microscope an Ediswan "Pointolite" lamp, 100 candle power, was used, the light passing through the usual condensing system to the 45° reflector in the microscope.

RESULTS—The measurements that have been made to date would indicate that this method has possibilities for research purposes, although it is not considered likely to have any particular value as a routine testing method. Many variable and unsatisfactory results were obtained during the early part of the work and changes in the apparatus were made to meet difficulties that developed. A single set of measurements will be cited to show the nature of the results. These measurements were made on a piece of carbon steel containing an insert of aluminium bronze, the specimen having been heated to 850° C. for 7 hrs. and cooled in the furnace. The appearance of the polished and etched section is shown in Fig. 3.

In the table each group of values represents a series of readings of the e. m. f. of the system for a given microscopic spot on the steel section, the values in-

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[1] *Proc. Roy. Soc.*, **72** (1903), 227.

[2] Lord Kelvin, *Phil. Mag.*, **46** (1898), 82; Hambeuchen, University of Wisconsin, *Engineering Bulletin* **2** (1901), 235; Jackson, *Trans. Am. Soc. Mech. Eng.*, **22** (1900–1901), 816.

[1] THIS JOURNAL, **12** (1920), 1090.

[2] *J. Am. Chem. Soc.*, **36** (1914), 2011.

creasing as the readings are repeated. In each group the value marked with an asterisk is the maximum value, the reading remaining constant to three decimals for 30 sec. The first column contains values, in volts, of the e. m. f. for various points on the ferrite ring X of Fig. 3. In the second and third columns are given values for various points on the body Y of the steel. For the last-named points, an effort was made to restrict the contact to ferrite grains. Where the grains were small it was not always possible to do this, but the results are not appreciably affected by contact of the solution with pearlite grains, since pearlite is a conglomerate of ferrite and cementite, and since ferrite is the more positive of the two substances.

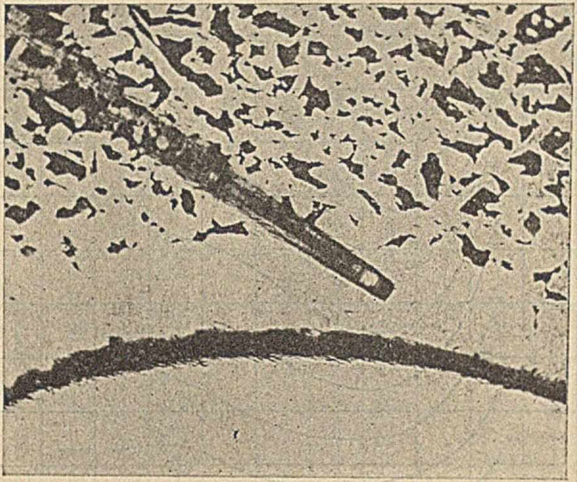
FIG. 2—GLASS CAPILLARY POINT APPLIED TO A FERRITE RING. × 50

TABLE I—E. M. F. IN VOLTS, FOR STEEL WITH ALUMINIUM BRONZE INSERT

Different Points on Ferrite Ring	Different Points on Body of Steel	Different Points on Body of Steel (*Cont.*)
0.438	0.481	0.506
0.456	0.483	0.510
0.471	0.486	0.514
*0.471	0.497	0.519
	0.560	*0.519
0.456	*0.560	
0.467		0.421
0.471	0.504	0.498
0.483	0.503	0.509
0.485	0.512	*0.509
*0.485	0.516	
	0.520	0.447
0.437	0.521	0.468
0.456	*0.521	0.475
0.457		*0.475
*0.457	0.494	
	0.510	0.510
0.379	0.537	0.512
0.435	0.541	0.514
0.459	0.543	0.518
0.464	*0.543	0.519
0.466		*0.519
*0.466	0.432	
	0.452	
0.451	0.500	
0.454	0.501	
0.478	*0.501	
*0.478		
	0.507	
	0.517	
	0.523	
Average of Maximum Values for Ferrite Ring	0.533	Average of Maximum Values for Body of Steel
	0.536	
	0.541	
	0.552	
0.471	*0.552	0.522

There is considerable variation between the maxima for the different groups in a given column. This, it would seem, might be expected, since we are dealing with a material whose composition must vary from point to point. Even upon the assumption that copper and aluminium have passed into the steel mass, thus causing the appearance of the ferrite ring, it is not to be supposed that the concentration of these metals in the ring is at all a constant quantity. The electrode potential would then be somewhat variable, and the e. m. f. of the system would vary accordingly.

Ferrite grains in the body of the piece, so far removed from the alloy insert as to preclude the possibility of contamination, are also undoubtedly impure. They probably contain most of the phosphorus and silicon of the steel, as well as traces of other impurities, and their electrode potentials also will vary.

Considering both of these probabilities it is yet significant that the starred values for the ferrite of the body of the steel are distinctly higher than those for the ferrite ring.

ELECTRODE POTENTIAL

Using 0.560 volt for the value for the calomel half-element, it will be seen that the electrode potentials for the metal, as calculated from these results, have negative values. The average for the ferrite ring is $0.471 - 0.560 = -0.089$ volt, and for the body of the piece, $0.522 - 0.560 = -0.038$ volt, a difference of about 0.05 volt. This is not in agreement with most of the values that have been found by others for iron. Walker and Dill[1] found the value 0.156 volt for unstrained Swedish iron in a ferrous sulfate solution, whose concentration was not stated. This value indicates that the solution was positive to the metal, the opposite of which is true in our measurements. Other recorded results vary somewhat from those obtained by Walker and Dill, but variations in purity, occluded gases, etc., are largely responsible.[2]

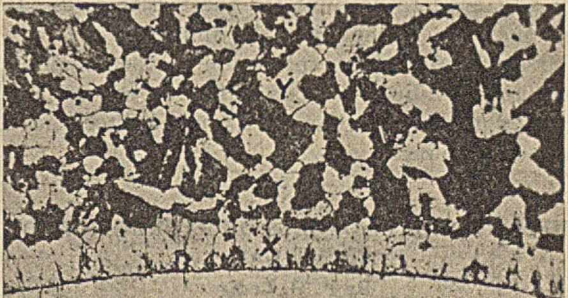

FIG. 3—STEEL ADJOINING AN INSERT OF ALUMINIUM BRONZE, HEATED FOR 7 HRS. AT 850° C. × 100

It was at first thought that this indicated an error in the method of reading, but a comparison of the electrode potential of a sample of polished and etched ingot iron made by the point-contact method above described and by immersion of the specimen in the electrolyte, shows that the immersion method gives

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[1] *Trans. Am. Electrochem. Soc.*, **11** (1907), 153.

[2] See also Richards and Behr, "The Electromotive Force of Iron, and the Effect of Occluded Hydrogen," Pub. Carnegie Inst., **1906**.

higher readings, more nearly in accord with the results of others for practically pure iron in ferrous sulfate. It will then be concluded, either (*a*) that the point-contact method does not give true equilibrium values, contact being made for too short a time, or (*b*) that surface tension or some similar influence consistently lowers the actual potential of the grain under observation. The latter hypothesis seems not unlikely, in view of the fact that in approximately the same time period the e. m. f. values for the system containing the immersed specimen of ingot iron were considerably higher than those obtained by point contact. It is not likely that absolute equilibrium has been reached in any case, but the starred values were not changing to the extent of 0.001 volt in 30 sec. Longer contact than a few minutes is not practicable, evaporation and oxidation then serving to render the results undependable.

SUMMARY

A method has been developed for measuring the electrode potential of a single grain or microscopic point on a metal specimen. Results so far obtained show lower values than are given when a pure metal is immersed according to the usual scheme. No reason for this has been demonstrated, but it is shown that fairly consistent values may be obtained on a given kind of material.

When the method is applied to a piece of steel containing a segregated ring of ferrite, produced by heating in contact with aluminium bronze, it is found that average values for the ferrite ring are 0.051 volt lower than for ferrite in the unaffected body of the steel. This indicates a different degree of purity for ferrite under the two conditions, and sustains the theory already advanced to account for the ferrite ring. It is hoped that the method may be improved so that it may be applied to the exploration of the regions adjoining nonmetallic inclusions in ferrite, as well as the segregated masses of ferrite often found in steels but not associated with inclusions.

INFLAMMABILITY OF JETS OF HYDROGEN AND INERT GAS[1]

By P. G. Ledig

BUREAU OF STANDARDS, WASHINGTON, D. C.

Received July 29, 1920

The purpose of the experimental work herein described was to determine the maximum amount of hydrogen which could be used with helium in balloons without losing the advantage of noninflammability. Preliminary experiments to determine the inflammability of a jet of hydrogen and inert gas under various conditions were made with hydrogen and nitrogen, in order to save helium. Later work showed that, as was supposed, there was not a great enough difference in the behavior of the gases to make it necessary to use helium throughout.

The gas mixtures were made up in a water-sealed gasometer (a meter prover) with a capacity of somewhat over 5 cu. ft. A scale on the tank was calibrated in tenths of a cubic foot. A large valve opened into a vertical cylindrical chamber about 10 cm. in diameter and 30 cm. long, with clamps at the open upper end by which steel orifice plates could be fastened in place. There were six of these orifice plates, 2 mm. in thickness, having circular orifices of 5, 10, 15, 20, 25, and 30 mm. diameter, respectively.

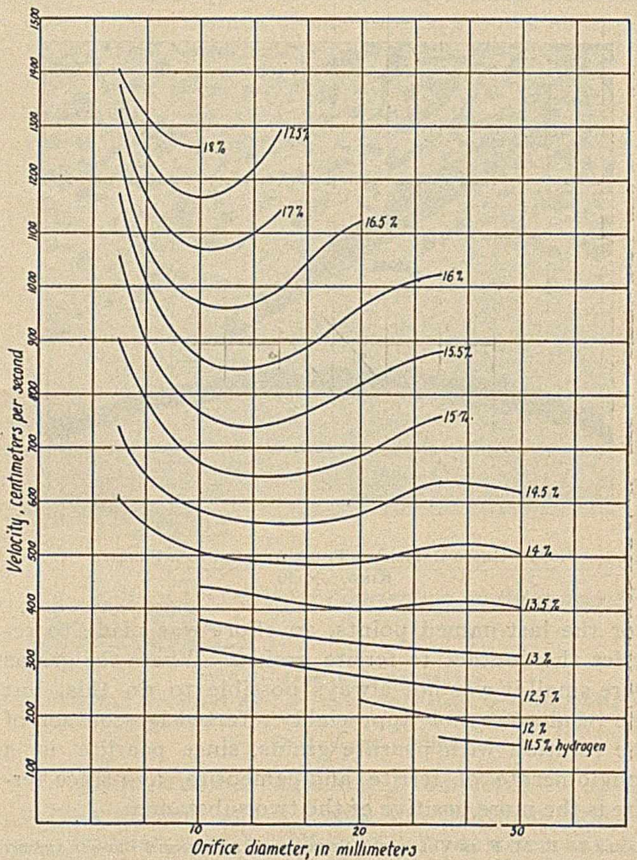

FIG. 1—RELATION OF BLOW-OFF VELOCITY TO ORIFICE DIAMETER AND HYDROGEN CONTENT

A gas mixture of approximately the composition desired was allowed to stand in the gasometer for a period of half an hour or more to permit diffusion of the hydrogen and nitrogen. The gas was then analyzed for hydrogen content, with an accuracy of 0.1 per cent. The orifice chamber was now swept out with this gas and the gas stream was then slowed down sufficiently to permit ignition or proof that the gas mixture would not burn in air. A small jet of burning coal-gas was used to ignite the gas stream. If the mixture burned, the valve was slowly opened until the velocity of the gas stream extinguished the flame by blowing it from the orifice. Since the hydrogen flame was practically invisible, it was usually found most convenient to judge this blowing-off point by sound. The flame fluttered more and more loudly as it approached the blowing-off velocity. After the flame had blown off, the valve was left open at the same position, and the gas velocity measured immediately by timing with a stopwatch the fall in the gas holder during the discharge of a definite quantity of gas. In practically all cases there was sufficient gas in the tank to make from three to five determinations with a single orifice.

[1] Published with permission of the Director of the Bureau of Standards.

By repeating the procedure with all the orifices and over ranges of composition from the lower limit of combustibility up to varying upper percentages of hydrogen (depending upon the orifice diameter), the curves of Fig. 1 were obtained. This shows the effect of changes of composition and orifice diameter upon the blow-off velocity of hydrogen-nitrogen mixtures.

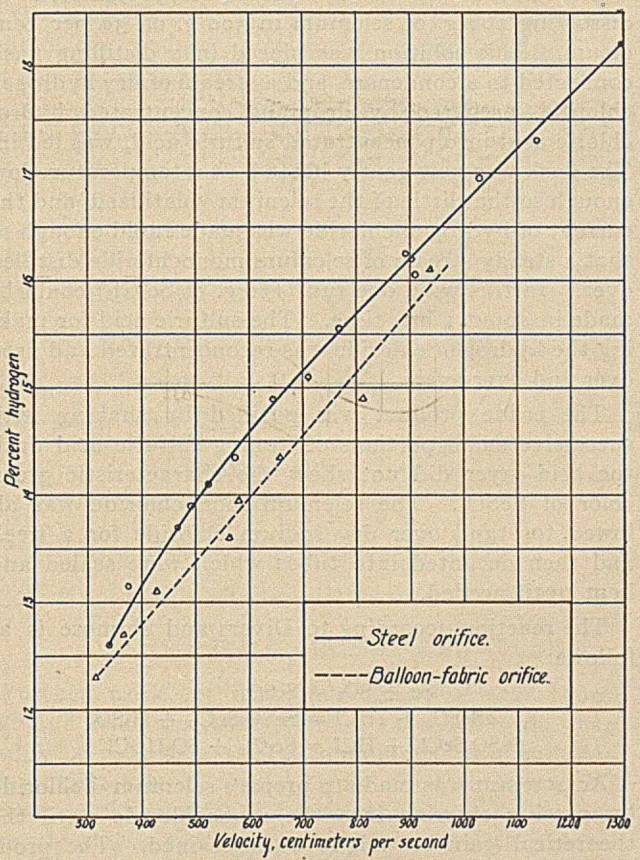

FIG. 2—EFFECT OF USING A BALLOON FABRIC ORIFICE, 10 MM. IN DIAMETER

It will be seen that, for gas mixtures near the inflammable limit, the velocity at which the flame is extinguished is practically the same for orifices from 10 to 30 mm. in diameter. It is certain that the velocity at which the flame is extinguished will be less and less affected by the size of the orifice the larger the size becomes. This is true because the only conceivable effect of the size of the orifice upon inflammability is due to the influence of one portion of the flame cap upon neighboring portions, and such mutual influence is rapidly eliminated as the size of the flame is increased.

In order to determine whether any great difference is produced by using balloon fabric instead of metal for orifice material, a series of tests was run with an orifice 10 mm. in diameter cut in standard dirigible fabric. Fig. 2 shows the results of these tests. The hole in the balloon fabric enlarged scarcely at all under the influence of the slight heat from these flames, even after a considerable number of determinations were made with it. A mica orifice gave results identical with those obtained with the steel orifice, which indicates that conduction of heat by the orifice plate has little or no effect upon the blowing-off velocity for orifices as large as those used.

In the final experiments, nitrogen was replaced by helium containing about 5.5 per cent of nitrogen. The 15-mm. steel orifice was used in this series of determinations. The curve for blow-off velocity follows quite closely that of the hydrogen-nitrogen mixtures (Fig. 3). There is a difference of about 2 per cent of hydrogen in the lower limit of inflammability, however, 12.5 per cent being the lower limit in the hydrogen-nitrogen mixtures, and 14.5 per cent being the lower limit in hydrogen-helium mixtures.

In order to obtain an idea of the pressures in a balloon which would produce the gas-stream velocities necessary to blow off a flame, a series of calculations was made upon the results shown in Fig. 3, using the following equation:

$$P_o = p \frac{1}{\left[\frac{-S^2}{2\,\theta\,C_p}\right]^{\frac{K}{K-1}}}$$

P_o = Pressure inside the orifice
p = Pressure outside the orifice
S = Gas-stream velocity (cm. per second)
θ = Absolute temperature of the gas
C_p = Specific heat of the gas at constant pressure (ergs per gram)
K = Ratio of the specific heats of the gas $\left(\frac{C_p}{C_v}\right)$

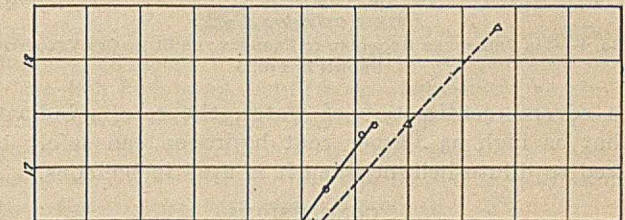

FIG. 3—COMPARISON OF BLOW-OFF VELOCITIES FOR HYDROGEN-NITROGEN MIXTURES WITH THOSE FOR HYDROGEN-HELIUM MIXTURES, 15 MM. ORIFICE

In Fig. 4 the pressures so computed are plotted against percentage of hydrogen in the gas mixtures. Since the gas pressures in a balloon are equivalent

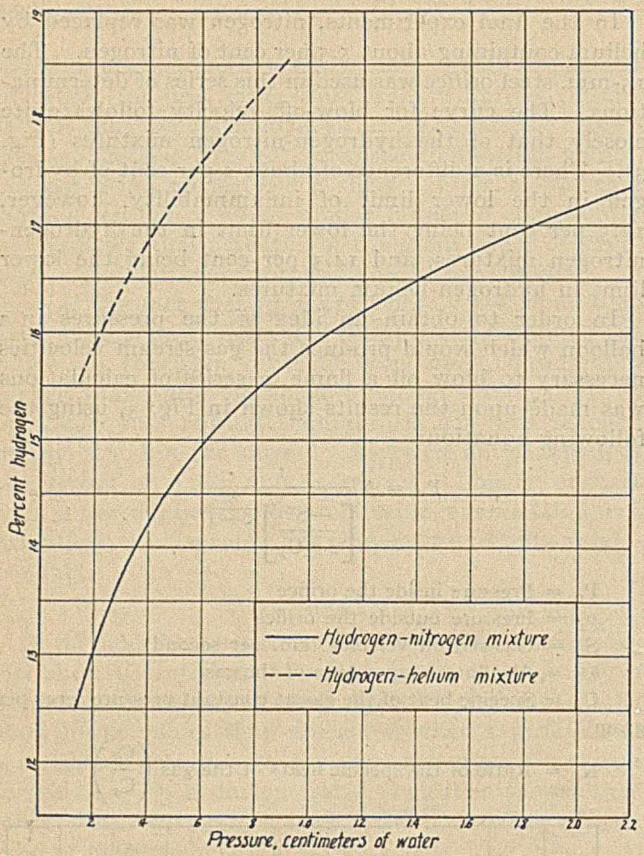

FIG. 4—GAS PRESSURES REQUIRED TO PRODUCE THE BLOW-OFF VELOCITIES SHOWN IN FIG. 3

to several centimeters of water, the results indicate that as high as 18 per cent hydrogen can safely be used to dilute helium when it is used in balloons.

CONCLUSIONS

1—Under the most favorable conditions, a jet of helium containing more than 14 per cent of hydrogen can be ignited in the air.

2—Eighteen to twenty per cent of hydrogen may be mixed with helium, without producing a mixture which will burn with a persistent flame when issuing from an orifice under the conditions prevailing in balloon practice.

3—More than 20 per cent of hydrogen in a hydrogen-helium mixture cannot be used in a balloon without sacrificing safety from fire.

THE REACTION BETWEEN SELENIUM MONOCHLORIDE AND ETHYLENE

By **F. H. Heath and Waldo L. Semon**
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

Received July 17, 1920

In the attempt to prepare the selenium analog of β,β'-dichloroethyl sulfide (mustard gas), it was necessary to prepare selenium monochloride and to attempt the preparation of selenium dichloride.

PREPARATION OF SELENIUM MONOCHLORIDE

The method of direct union of chlorine and selenium suggested by Beckmann[1] was found to give a product too impure for use, since it contained much free selenium and considerable selenium tetrachloride. The reaction of selenium in sulfuric acid and hydrogen chloride as reported by Divers and Shimose[1] yielded a very good product, but was much too slow for the preparation of large quantities of selenium monochloride.

The method, as finally worked out, consisted in dissolving 100 g. of selenium in 300 g. of 30 per cent oleum. This solution was placed in a distilling flask connected to a condenser, and a stream of dry hydrogen chloride, prepared by dropping concentrated hydrochloric acid into concentrated sulfuric acid, was led in. The flask was now gently heated, at a temperature low enough so that little of the selenium volatilized, and the current of hydrogen chloride was made rapid enough so that a steady stream of selenium monochloride distilled over. In this way, one run (130 g. of Se_2Cl_2) could be made in about 2 hrs. time. The sulfuric acid for making the hydrogen chloride was reconcentrated and used over and over again.

The crude product was purified by shaking with successive small portions of fuming sulfuric acid until the acid layer did not show the characteristic green color of $SeSO_3$. The selenium monochloride was allowed to stand over dry sodium chloride for a week and then decanted into tubes which were sealed and kept until needed.

The reaction according to Divers and Shimose is as follows:

$$Se + SO_3 = SeSO_3$$
$$2SeSO_3 + 2HCl = SeSO_3SeCl_2 + H_2SO_3$$
$$SeSO_3SeCl_2 + HCl = Se_2Cl_2 + SO_2HOCl$$

An attempt was made to prepare selenium dichloride by passing chlorine into the monochloride until the theoretical gain in weight was obtained. The product consisted of a mixture of selenium monochloride and selenium tetrachloride and was found to react with ethylene the same way as the monochloride, but with smaller yields.

REACTION BETWEEN ETHYLENE AND SELENIUM MONOCHLORIDE

On leading a slow stream of ethylene into selenium monochloride, the liquid became warm, selenium was precipitated, and hydrogen chloride was evolved. When the reaction was complete, hot chloroform was added, and the selenium was filtered off. On cooling, long, white, needle-like crystals were precipitated. Upon recrystallization from chloroform they had the characteristic selenium odor, and were found to melt with decomposition at 118° (uncorr.). On analysis the following results were obtained:

	No. of Analyses	Found Per cent	Theory for $C_4H_6Cl_4Se$ Per cent
Carbon	1	18.1	17.5
Hydrogen	1	2.9	2.2
Chlorine	4	51.7	51.6
Selenium	2	28.56	28.8
TOTAL		101.26	100.1

This shows the compound to be $C_4H_6Cl_4Se$.

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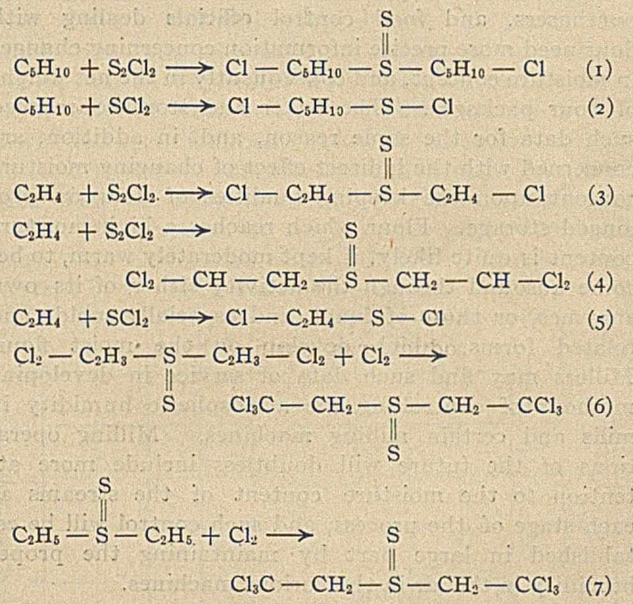
[1] *Z. physik. Chem.*, **70**, 1.

[1] *Chem. News*, **49** (1894), 212.

When ethylene was led into a carbon tetrachloride solution of selenium monochloride or into the attempted selenium dichloride, the same product was obtained, but in smaller yields.

To establish the structural formula of $C_4H_6Cl_4Se$, we may reason by analogy from the sulfur compounds. In the following equations may be found a brief resumé of the work done by Guthrie,[1] as interpreted in the light of our modern knowledge of chemistry.



$$C_5H_{10} + S_2Cl_2 \longrightarrow Cl - C_5H_{10} - \overset{S}{\overset{\|}{S}} - C_5H_{10} - Cl \quad (1)$$

$$C_5H_{10} + SCl_2 \longrightarrow Cl - C_5H_{10} - S - Cl \quad (2)$$

$$C_2H_4 + S_2Cl_2 \longrightarrow Cl - C_2H_4 - \overset{S}{\overset{\|}{S}} - C_2H_4 - Cl \quad (3)$$

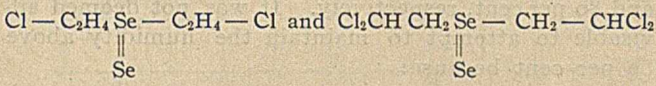
$$C_2H_4 + S_2Cl_2 \longrightarrow Cl_2 - CH - CH_2 - \overset{S}{\overset{\|}{S}} - CH_2 - CH - Cl_2 \quad (4)$$

$$C_2H_4 + SCl_2 \longrightarrow Cl - C_2H_4 - S - Cl \quad (5)$$

$$Cl_2 - C_2H_3 - \underset{S}{\underset{\|}{S}} - C_2H_3 - Cl_2 + Cl_2 \longrightarrow Cl_3C - CH_2 - \underset{S}{\underset{\|}{S}} - CH_2 - CCl_3 \quad (6)$$

$$C_2H_5 - \overset{S}{\overset{\|}{S}} - C_2H_5 + Cl_2 \longrightarrow Cl_3C - CH_2 - \overset{S}{\overset{\|}{S}} - CH_2 - CCl_3 \quad (7)$$

Further work by Frederick Kont-Norwall[2] shows that one selenium from selenium monochloride may readily be split off from its compounds, as is sulfur in the manufacture of mustard gas. Equations 3 and 4 show how the reaction between ethylene and selenium monochloride may quite probably run. Although we have no evidence of the existence of the compounds



$$Cl - C_2H_4\underset{Se}{\underset{\|}{Se}} - C_2H_4 - Cl \text{ and } Cl_2CH\,CH_2\underset{Se}{\underset{\|}{Se}} - CH_2 - CHCl_2$$

it is quite probable that they may be formed and the final product be $Cl_2CH.CH_2.Se.CH_2.CHCl_2$. Equations 6 and 7 show the symmetry of the atom, and by analogy the selenium compound is assumed to be likewise symmetrical.

PHYSIOLOGICAL EFFECTS

Although the physiological effects of this compound have not been studied, the experimenter has been continually troubled with water blisters on his hands while doing this work. A person working with this compound is also liable to be overcome with a sense of drowsiness. Whether this be due to the compound or to some by-product is not known.

CONCLUSIONS

1—A simple method for the preparation of selenium monochloride has been described.

2—$C_4H_6Cl_4Se$ has been prepared and it has been shown to be symmetrical tetrachlorodiethyl selenide.

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[1] *J. Chem. Soc.*, **12**, 109; **13**, 35, 135.

[2] *Oesterr. Chem.-Ztg.*, **16**, 288.

NOTE ON CATALYSIS IN THE MANUFACTURE OF ETHER[1]

By Hugo Schlatter

Hercules Powder Co., Wilmington, Delaware

Received August 18, 1920

Senderens,[2] discussing the action of aluminium sulfate as a catalyst in the manufacture of ether, states that the addition of about 5 per cent of the anhydrous sulfate to the usual mixture of sulfuric acid and alcohol lowers the temperature at which regular and rapid evolution of ether takes place from 140° C. to 130° C. He explains this action by assuming the formation of a double aluminium ethyl hydrogen sulfate ($Al_2(SO_4)_3.SO_4HC_2H_5$), which breaks up at a lower temperature than ethyl sulfuric acid.

Although in plant operation the temperature of the still at which regular and rapid evolution of ether takes place is about 125°, it was thought of interest to determine whether the addition of aluminium sulfate would result in lowering this temperature still further, or in increasing the capacity of the still. During the war any increase in the capacity of existing apparatus was of supreme importance.

A small, glass, ether still with the necessary column and condensers was charged with a mixture of sulfuric acid and alcohol. After the evolution of ether had started, alcohol was fed into the still below the surface of the liquid at a rate corresponding to the ether produced. Senderens' statement, that evolution does not become regular until a temperature of 140° is reached, was confirmed. Amounts of aluminium sulfate varying from 3 to 10 per cent by weight were introduced into the still in subsequent runs, and it was found that with 5 or 10 per cent of aluminium sulfate the temperature was lowered to 130°.

A somewhat larger still of 1.5-gal. capacity was then constructed of lead and equipped with a steam heating coil, so as to approach factory conditions as closely as possible. Two runs of about 50 hrs. duration were made, one with and one without the addition of 5 per cent by weight of aluminium sulfate. The temperatures throughout the two runs were the same as in factory operation, *i. e.*, from 120° to 125°, and there was no difference in the net yield of the two runs.

When the still was opened after the completion of the run, it was found that severe pitting of the coils had occurred when aluminium sulfate was present, possibly owing to electrolytic action between the lead of the coils and the aluminium sulfate. In both cases there was a sludge of sulfates.

A short test was also made in the original glass still with broken porcelain. In this case the temperature at which regular evolution occurred was lowered to the same temperature (130°) as with aluminium sulfate in the glass still.

It is apparent, therefore, that aluminium sulfate offers no advantages over the lead sulfate which is normally present in lead ether stills, but is actually harmful, since it causes pitting and rapid failure of the coils. The action of lead sulfate could be explained

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[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] *Compt. rend.*, **151** (1910), 392.

by the formation of a double salt ($PbSO_4.SO_4HC_2H_5$), but the action of broken porcelain rather seems to disprove this theory and inclines us to the view that the rapid and regular evolution is due to physical or surface action. This view is strengthened by the fact that irregular evolution of ether actually commences at the lower temperature, even if no lead sulfate is present.

The observations recorded are interesting, also, because the choice of lead for the construction of a manufacturing still, which was made necessary by the character of the reagents, resulted in an improvement in the process that could not have been foreseen from laboratory experiments in glassware, and in fact had heretofore been largely overlooked.

Credit is due to Mr. W. M. Billing for carrying out the laboratory work.

THE HYGROSCOPIC MOISTURE OF FLOUR EXPOSED TO ATMOSPHERES OF DIFFERENT RELATIVE HUMIDITY[1,2]

By C. H. Bailey[3]

Division of Agricultural Biochemistry, Minnesota Agricultural Experiment Station, St. Paul, Minn.

Received July 30, 1920

It has long been known that cereals and cereal products are hygroscopic, and that their moisture content may be altered by varying the conditions of exposure. Brewer (1883) details certain experiments which establish this property. Other investigators, including Willard (1911), Neumann (1911), Guthrie and Norris (1912), Sanderson (1914), Swanson, Willard and Fitz (1915), and Stockham (1917), have studied the changes in weight and moisture content of stored flour. In none of these experiments, save those of Stockham, have the atmospheric conditions apparently been controlled throughout the period of exposure. Guthrie and Norris (1912) recorded the atmospheric humidity each day during the period that the flour was under observation, but their readings were apparently taken at one particular time each day, and hence do not represent the mean humidity for the several 24-hr. periods. Even had the latter been determined, it is doubtful if the hygroscopic moisture of the flour could be regarded as in equilibrium with the mean humidity of the atmosphere, when the humidity fluctuated as suddenly and violently as appears to have been the case.

Stockham (1917) reports the moisture content of wheat, bran, shorts, and flour exposed in a "saturated" and "dry" atmosphere, but did not employ any degrees of atmospheric humidity between these extremes. He found that a composite sample of flour exposed in a "still, saturated" atmosphere at a temperature of 23° C. (see p. 109) reached a maximum moisture content of 28.74 per cent in 9.12 days, at which time it was moldy. In a saturated atmosphere at 0° a moisture content of 34.78 per cent was reached in 17 days, which he states was not the maximum.

SIGNIFICANCE OF MOISTURE CONTENT OF FLOUR

It seemed desirable to ascertain the moisture content of flour in atmospheres of differing but constant humidity, after a period of exposure sufficiently long to permit the hygroscopic moisture of the flour to reach equilibrium with the atmosphere. Such data would be of service in a number of ways. Shippers, purchasers, and food control officials dealing with flour need more precise information concerning changes in moisture content, and consequently in the net weight of flour packages. The baker and storekeeper need such data for the same reason, and, in addition, are concerned with the indirect effect of changing moisture content upon the keeping qualities of flour on prolonged storage. Flour which reaches a high moisture content is quite likely, if kept moderately warm, to become unsound through the activity either of its own enzymes, or those of fungi, and especially molds and related forms, which develop on the moist flour. Millers may find such data of service in developing methods of controlling the atmospheric humidity in mills and certain milling machines. Milling operations of the future will doubtless include more attention to the moisture content of the streams at each stage of the process, and such control will be established in large part by maintaining the proper humidity in the air in the various machines.

METHOD OF PROCEDURE

The humidity of the atmosphere to which flour was exposed was controlled by contact with the surface of sulfuric acid solutions. These solutions were prepared after the Reynault tables in Landolt, Börnstein and Roth's "Tabellen."[1] Four solutions were prepared, which were intended to afford humidities of 30, 50, 70, and 80 per cent, respectively. It was not deemed advisable to attempt to maintain the humidity above 80 per cent because:

(*a*) The flour is apt to mold in very damp atmospheres.

(*b*) In most parts of the United States an atmospheric humidity in excess of 80 per cent is not likely to be maintained for a prolonged period.

(*c*) It becomes more difficult to maintain the humidity at a constant level when in excess of 80 per cent.

Two samples of flour were used in these studies—a patent and a second clear flour. Their chemical composition is shown in Table I.

TABLE I—COMPOSITION OF FLOURS USED IN HYGROSCOPIC MOISTURE STUDIES

		CALCULATED TO DRY BASIS		
SAMPLE	MOISTURE Per cent	Crude Protein (N × 5.7) Per cent	Ash Per cent	Acidity (as Lactic) Per cent
Patent	8.71	12.44	0.47	0.159
Second clear	9.92	16.46	2.38	0.781

Five grams of each of these flours were placed in tared, flat-bottomed, aluminium drying dishes, having a diameter of 50 mm. This quantity of flour filled the dishes to a depth of 5 to 6 mm. The dishes were placed in desiccators, the lower part of which was filled with the appropriate sulfuric acid solution. The several desiccators were set in a thermostat having a

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[1] Published with the approval of the Director as Paper No. 214, Journal Series, Minnesota Agricultural Experiment Station.

[2] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[3] With the coöperation of Miss Isabel Everts.

[1] 4th Edition, **1912**, p 426.

a temperature of 25°. This was the lowest temperature which could be constantly maintained in the basement rooms of the laboratory building during the spring and early summer months.

Preliminary studies indicated that it required 6 to 8 days for the flour to reach equilibrium in moisture content. The time doubtless hinges in part on the difference between the initial moisture of the flour and that which it will ultimately attain. To insure that ample time was afforded, the dishes (all tests being carried out in duplicate) were left undisturbed for 8 days, weighed, returned to the chambers for 2 days more, and again weighed. The difference between the first and second weighings was usually small. The dishes with their contents were dried to constant weight at 100°C. *in vacuo*, and the weight of the empty dish being known, the calculation of the initial and final moisture content of the flour was then possible.

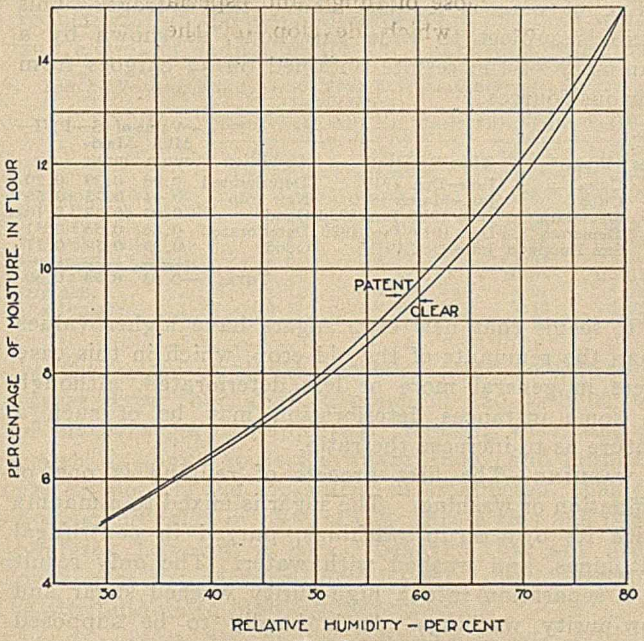

Fig. 1

At the time the dishes were finally removed from the desiccators, a portion of the sulfuric acid was drawn off and its specific gravity at once determined. From this, the percentage of H_2SO_4 could be ascertained, and the vapor pressure and relative humidity computed through the use of the tables mentioned herewith. Since it was not convenient to prepare sulfuric acid solutions of concentrations which would give exactly the humidity desired at the close of the experiments, small variations from the desired humidity were found in most cases. These deviations were always less than one per cent, in terms of relative humidity.

In Table II and Fig. 1 are shown the percentages of moisture in the patent and clear flours exposed to atmospheres of approximately 30, 50, 70, and 80 per cent relative humidity. While the differences between the two grades of flour are small, they are in the direction of a slightly higher hygroscopicity on the part of the patent grade. Stockham (1917) had previously shown (page 105) a difference in the hygroscopic moisture of starches prepared from patent and clear flours, those from the patent containing more moisture when they were exposed under identical conditions. The curves are of the shape of a simple parabola, which, if extrapolated to 100 percent humidity, would give values in terms of hygroscopic moisture not far different from those reported by Stockham for the flours exposed in a "saturated" atmosphere.

TABLE II—HYGROSCOPIC MOISTURE OF PATENT AND SECOND CLEAR FLOURS IN CONTACT WITH ATMOSPHERES OF VARIOUS HUMIDITIES AT 25° C. (78° F.)

Relative Humidity of Atmosphere at 25° C. Per cent	Moisture of Flour	
	Patent Per cent	Second Clear Per cent
80.0	15.00	15.00
69.8	12.05	11.65
50.3	7.93	7.81
29.4	5.18	5.11

The question at once arises as to how rapidly these flours change in moisture content with variations in the humidity of air to which they are exposed. That the response is rapid may be deduced from the experiments of Guthrie and Norris (1912). The exact rate must depend upon a number of variables, however, including the size and shape of the package in which flour is contained, the material from which it is manufactured, the extent of circulation of air about the package, and possibly other factors of minor importance. It appeared impossible to develop this phase of the investigation adequately at this time, and the study of rate of response must be deferred to a later date. Such data as were secured in certain of our preliminary studies indicate, as might be anticipated, that a dry flour placed in a humid atmosphere (or *vice versa*) changes rapidly the first 3 days, and much more slowly the next 3 days, after which, if exposed in thin layers, there is little further change.

CONCLUSIONS

Flour responds readily to changes in the humidity of surrounding air, the rate at which equilibrium in moisture content is approached depending apparently upon conditions of exposure.

Hygroscopic moisture in flour in equilibrium with atmospheric humidity at 25° C. ranges from a little more than 5 per cent of moisture at 30 per cent relative humidity to 15 per cent of moisture at 80 per cent relative humidity.

Curves representing the relation between hygroscopic moisture (ordinates) and relative humidity (abscissae) have the shape of a simple parabola, thus indicating that hygroscopic moisture does not increase at a uniform rate when in equilibrium with an increasing atmospheric humidity.

Flour testing laboratories engaged in analyzing fresh flour containing 12 to 13 per cent of moisture will experience no appreciable change in the moisture content of such flour if the relative humidity of the laboratory atmosphere is maintained in the neighborhood of 70 per cent.

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CHANGES IN THE POLARIZING CONSTANTS OF SUGARS DURING REFINING[1]

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It is the purpose of this paper to discuss the changes taking place in the relationship between polarization, true sucrose, and invert sugar during the refining of raw sugar, to determine, if possible, the causes of these changes, and to point out their practical significance. As pointed out by Dr. Browne,[2] the percentage of true sucrose in a mixture of sucrose with pure invert sugar, consisting of equal parts of dextrose and levulose, will exceed the polarization at 20° C. by about three-tenths of the percentage of invert sugar. That is,

$$\frac{S - P}{I} = 0.30$$

where S represents the percentage of sucrose, P the polarization, and I the percentage of invert sugar. The factor will vary very slightly with the concentrations of sucrose and invert sugar, but a very small deviation from equality in the proportions of dextrose and levulose in the invert sugar will very greatly alter its value, because of the wide difference in the rotations of these two sugars. A value of $(S - P)/I$ above 0.30 indicates excess of levulose; a value less than 0.30, an excess of dextrose. Dr. Browne discusses the influence of temperature, maturity of cane, methods of manufacture, and length of storage of raw sugar upon the value of this ratio, and mentions the fact that in the process of refining its value is very materially reduced, and gives analyses of soft sugars and refiners' sirup, in support of this assertion.

EXPERIMENTAL PART

In Table I is shown an analysis of a cargo of Cuban raw centrifugal sugar of uniform quality and all one mark, together with the average analyses of soft refined sugar and refiners' barrel sirup produced from it. These particular analyses are selected for the purposes of the discussion because they are quite typical and because the refinery started melting this cargo following a shutdown from which practically no stock in process was brought forward, and melted this cargo exclusively for a considerable period, so that it is quite certain that the three analyses are interrelated. Dr. Browne's observation of the reduction of the value of $(S - P)/I$ is very strikingly affirmed.

TABLE I—ANALYSIS OF CUBAN RAW CENTRIFUGAL SUGAR AND OF SOFT REFINED SUGAR AND REFINERS' BARREL SIRUP PRODUCED THEREFROM

	RAW SUGAR	SOFT SUGAR	REFINERS' SIRUP
ANALYSES WET			
Polarization at 20° C.	95.87	88.47	38.40
Sucrose Clerget	96.42	88.74	40.60
Water by Drying	1.05	5.29	19.57
Invert	1.25	3.51	22.99
Insoluble	0.16	...	...
Soluble Ash	0.66	1.24	8.13
Soluble Organic	0.46	1.22	8.71
EX-WATER AND INSOLUBLE			
Polarization	97.04	93.41	47.74
Sucrose Clerget	97.59	93.70	50.48
Invert	1.27	3.71	28.58
Ash	0.67	1.31	10.11
Organic	0.47	1.28	10.83
IMPURITIES			
Invert	52.7	58.8	57.7
Ash	27.8	20.8	20.4
Organic	19.5	20.4	21.9
RATIOS			
Invert ÷ Sucrose × 100	1.30	3.95	56.6
Invert ÷ Ash	1.89	2.83	2.83
(S — P)/I	0.44	0.077	0.096

The value has fallen from 0.44 in the raw sugar to 0.077 in the soft sugar and 0.096 in the sirup. The value of 0.44 is a little above the average. This ratio is subject to wide variations, as shown by a summary of the results obtained on 32 cargoes from various sources.

No. Cargoes	From	Time Received	Condition	—Value of (S—P)/I— Minimum	Maximum	Av.
8	Cuba	June–Dec. 1919	Deteriorated	0.08	0.29	0.20
6	Cuba	Jan.–March 1920	New crop	0.44	0.73	0.55
10	Demerara	June 1919–Jan. 1920	Good	—0.03	0.34	0.16
2	Demerara	Dec. 1919–Jan. 1920	Deteriorated	0.48	0.55	0.51
6	San Domingo	June–Oct. 1919	Good	0.23	0.59	0.37
			TOTAL	—0.03	0.73	0.30

It seems that new crop sugars have higher values than the remnants of the old crop, which in this case were in general more or less deteriorated, although in some instances deterioration may be of such a nature as to increase the ratio.

WASHING—The first process of refining is one of affination or washing. The sugar is mixed to a magma with its own sirup washings, purged in centrifugal machines, and washed with water. The only result is a separation into a high-purity washed sugar and low-purity washings. It is hardly to be supposed that any change in the value of $(S - P)/I$ would take place here, though it is possible that it might differ somewhat in washed sugar and washings, since the impurities in the sirup are those of the molasses adhering to the grain, and those in the washed sugar those in the grain itself. In the latter the invert is lower and the organic higher. The analyses in Table II would indicate that there is no great change of the $(S - P)/I$ ratio in the process of affining. The determination of the ratio with great accuracy is impossible in very high-purity material such as washed sugar, since a trifling error in polarization or Clerget, say, 0.05 degree, makes a large error in $(S - P)/I$. The washings, too, being very highly colored, present some difficulties in a Clerget determination, but the

TABLE II—ANALYSIS OF FILTERED SOLUTIONS OF CUBAN RAW SUGAR AND OF WASHED SUGAR AND CENTRIFUGAL WASHINGS PRODUCED THEREFROM

	Raw Sugar	Washed Sugar	Centrifugal Washings
Dry Polarization	96.37	98.77	78.05
Dry Clerget	96.91	98.98	80.56
Dry Invert	1.20	0.43	8.35
Dry Ash	0.62	0.19	3.62
Dry Organic	1.27	0.40	7.47
(S — P)/I	0.45	0.49	0.30

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[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] In a paper entitled "Influence of Conditions upon the Polarizing Constants of Sugar Cane Products," read at the 56th Meeting of the American Chemical Society, Cleveland, Ohio, September 10 to 13, 1918.

most approved methods were used and usual sources of error eliminated as far as possible.

DEFECATION—After the washing process both sugar and washings are defecated with lime and phosphoric acid at a temperature of 180° F. and left slightly alkaline to litmus. The concentrated, bone-black filter sweet water, or char water, and the concentrated bag-filter flush water, or scum water, are also thus treated and then filtered through bag filters. Table III shows no change for (S — P)/I for washed sugar from the time of reaching the blow-ups until through the bag filters. Table IV, however, shows a slight reduction from the defecation for scum and char water, and a greater reduction for the centrifugal washings. In the latter case, the material after defecation is rather more than slightly alkaline, and a slight loss of invert sugar is indicated. Heating with lime, of course, is known to destroy invert sugar, and doubtless the levulose is the ingredient most affected, thus reducing the value of (S — P)/I. From this and other analyses, however, it is not believed that any great portion of the decrease in (S — P)/I during refining is attributable to blow-up defecation.

TABLE III—ANALYSIS OF CENTRIFUGALLY WASHED RAW SUGAR BEFORE DEFECATION AND AFTER DEFECATION AND BAG FILTRATION

	Before Defecation	After Filtration
Brix	61.25	60.62
Dry Polarization at 20° C.	98.67	98.74
Dry Sucrose Clerget	98.81	98.89
Dry Invert	0.43	0.46
Dry Ash	0.25	0.23
Dry Organic	0.51	0.42
(S — P)/I	0.33	0.33

TABLE IV—ANALYSIS OF LOW TEST MATERIAL BEFORE AND AFTER DEFECATION

	Mixed Scum and Char Water		Centrifugal Washings	
	Before Defecation	After Defecation	Before Defecation	After Defecation
Alkalinity at 32° Bé	(0.001 *N* Acid)	0.009 *N*	0.006 *N*	0.023 *N*
Brix (Diluted and Filtered)	40.70	37.50	32.50	30.40
Dry Polarization	78.67	78.85	77.08	77.53
Dry Sucrose Clerget	78.87	78.99	78.83	78.39
Dry Invert	6.24	6.37	10.68	10.55
Dry Ash	4.72	4.80	3.01	3.13
Dry Organic	10.17	9.84	7.48	7.93
(S — P)/I	0.031	0.021	0.16	0.081

After use, the bag filters are flushed, in this case with hot water only, producing a light material known as scum water. The mud removed from the bags is diluted with water, limed, and heated to a high temperature, and filter-pressed, yielding press water. Table V shows comparative analyses of the centrifugal washings last on the bag filters, the scum water, and the press water. A decrease in the ratio is to be noted, the decrease being again accompanied by loss of invert. In the case of the press water, the invert has been practically all destroyed by the liming and heating, and, as would be expected, the polarization equals the Clerget, and (S — P)/I is zero. As only a small portion of the melt is handled as scum water or press water, however, we have to look further for the main cause of the decrease of the ratio.

TABLE V—ANALYSIS OF CENTRIFUGAL WASHINGS BEFORE DEFECATION SCUM WATER, AND PRESS WATER

	Centrifugal Washings	Scum Water	Press Water
Brix	57.40	18.20	5.15
Alkalinity by $Ca(OH)_2$	0.014 *N*	0.004 *N*	0.010 *N*
Dry Polarization at 20° C.	78.56	79.68	67.38
Dry Sucrose Clerget	80.94	80.38	67.38
Dry Invert	7.77	5.65	0.33
Dry Ash	4.10	4.56	10.25
Dry Organic	7.19	9.41	22.04
(S — P)/I	0.31	0.12	0.00

TABLE VI—ANALYSIS OF BAG-FILTERED MATERIAL BEFORE AND AFTER TREATMENT WITH FRESH BONE-BLACK

	Washed Sugar		Mostly Scum and Char Water	
	Before Treatment	After Treatment	Before Treatment	After Treatment
Brix	60.85	57.85	56.70	...
Dry Polarization	98.77	99.17	86.95	91.19
Dry Sucrose Clerget	98.87	99.15	87.11	90.80
Dry Invert	0.47	0.31	5.91	5.11
Dry Ash	0.24	0.13	2.35	1.26
Dry Organic	0.42	0.41	4.63	2.83
Invert Per cent Impurities	41.6	36.5	45.8	55.5
Ash Per cent Impurities	21.2	15.3	18.2	13.7
Organic Per cent Impurities	37.2	48.2	36.0	30.8
(S — P)/I	+0.21	—0.06	+0.027	—0.076

BONE-BLACK FILTRATION—Table VI shows a change in (S — P)/I on washed sugar filtered through bone-black, from +0.21 to —0.06, and on low-test bag-filtered material treated with fresh bone-black in a laboratory test from +0.027 to —0.076. It would seem that here is the real cause for the change in (S — P)/I during refining. In every test it has been found that in the case of the material first off the bone-black the polarization always exceeds the Clerget. Table VII gives progressive analyses of the various materials going on a bone-black filter and of roughly equivalent portions coming off. The value of (S — P)/I is greatly reduced on the first material, washed sugar, and progressively less so on the granulated sirups and char-filtered liquor following. The averages show a considerable loss for the whole operation. It is also to be noted that low material put on fresh bone-black, as in Table VI, suffers a large decrease in (S — P)/I, but when put on the end of a used filter the ratio is but little changed. Another point of interest is that invert is absorbed from first material and given up to later material, the whole operation resulting in no loss of invert. In this test there appears to be a slight loss of invert, but numerous other tests of like nature have shown a good balance, but always with the same transfer from first material to later material. The significance of this invert absorption will be treated shortly.

The same conclusions regarding the relation of char filtration to (S — P)/I are drawn from the analyses of three grades of soft sugar shown in Table VIII. The light yellows, boiled from liquor early off the char filters, show negative values for (S — P)/I, the brilliants boiled from later liquor show positive values, and the darks still higher values. The average soft sugar of Table I, mostly brilliants with small amounts of light and darks, shows a value in agreement with Table VIII. The high invert per cent of impurities on lights is not because invert has not been absorbed, but because the other impurities, ash and organic, have been absorbed to a much greater extent.

Subsequent to char filtration there appears to be no change in (S — P)/I. The average value for all the material off the filters is not greater than the average value in final soft sugars and barrel sirup. In Table I the value for sirup exceeds that for soft sugars because there is some light yellow, with its negative value of (S — P)/I, mixed into the average soft.

TABLE VII—ANALYSES OF MATERIAL GOING ON AND COMING OFF A BONE-BLACK FILTER

Going on Filter

MATERIAL	Washed Sugar		Granulated Sirup	Char-Filtered Liquor	Heavy Char Water	Weighted Average
Gallons	13,860	....	3,600	8,280	1,440	27,180
Solids Per cent of Total on	50.54	....	13.91	30.37	5.18	100.00
Brix	58.85	....	62.45	59.35	58.35	59.54
Alkalinity	0.003 *N*	....	0.002 *N*	0.003 *N*	0.006 *N*	0.003 *N*
Color	41.0	....	45.0	45.0	110.0	45.0
Dry Polarization	98.56	....	91.59	90.25	85.00	94.31
Dry Sucrose Clerget	98.59	....	91.75	90.47	85.36	94.44
Dry Invert	0.46	....	5.09	5.31	5.67	2.90
Dry Ash	0.29	....	1.38	1.73	3.57	1.05
Dry Organic	0.66	....	1.78	2.49	5.40	1.61
Invert Per cent Impurities	32.9	....	61.7	55.7	38.8	52.2
Ash Per cent Impurities	20.7	....	16.7	18.2	24.4	18.9
Organic Per cent Impurities	46.4	....	21.6	26.1	36.8	28.9
(Invert ÷ Sucrose) × 100	0.47	....	5.55	5.87	6.65	3.07
Invert ÷ Ash	1.59	....	3.70	3.06	1.59	2.76
(S — P)/I	0.07	....	0.031	0.044	0.063	0.045

Coming off Filter

MATERIAL	Washed Sugar	Mostly Washed Sugar	Granulated Sirups and Char-Filtered Liquor		Sweet Waters	Weighted Av. Up to "in Waste"
Gallons	10,660	2,660	3,550	10.240	3,260	30,370
Solids Per cent of Total off	38.83	9.93	13.14	36.30	1.80	100.00
Brix	59.55	60.90	60.50	57.90	9.05	53.81
Alkalinity	0.002 *N*	0.1002 *N*	0.002 *N*	0.002 *N*	(0.001 *N* Acid)	0.002 *N*
Color	1.0	5.0	11.0	20.0	9.0	10.0
Dry Polarization	99.45	97.78	94.88	90.33	60.77	94.68
Dry Sucrose Clerget	99.32	97.68	94.83	90.54	60.77	94.69
Dry Invert	0.28	1.50	3.42	5.46	4.85	2.77
Dry Ash	0.13	0.31	0.79	1.76	8.61	0.98
Dry Organic	0.27	0.51	0.96	2.24	25.77	1.56
Invert Per cent Impurities	41.0	64.5	66.1	57.7	12.4	52.2
Ash Per cent Impurities	18.5	13.5	15.3	18.6	21.9	18.5
Organic Per cent Impurities	40.5	22.0	18.6	23.7	65.7	29.3
(Invert ÷ Sucrose) × 100	0.28	1.53	3.61	6.03	7.98	2.93
Invert ÷ Ash	2.21	4.79	4.31	3.10	0.56	2.83
(S — P)/I	—0.48	—0.067	—0.015	+0.038	0.00	+0.004

The boiling in vacuum pans does not affect the ratio, if there is no inversion. Inversion, here or elsewhere, would presumably increase the ratio by addition of true invert sugar with its normal value of 0.30. That this is the case is shown in an exaggerated manner by the analysis in Table IX of a table sirup made by deliberate inversion of char-filtered liquor. (S—P)/I is 0.282 or, as would be expected, almost up to the theoretical value. A less exaggerated case is shown in Table X, where some char-filtered liquor was purposely submitted to slight inversion. The ratio has increased from 0.029 to 0.119. A subsequent treatment with bone-black reduced the ratio somewhat, but not to the original value. The value of this ratio is therefore a good indication of refinery performances.

TABLE VIII—ANALYSES OF LIGHT, BRILLIANT, AND DARK SOFT REFINED SUGARS

Lot No.	M 231	O 271	M 234	O 621	M 197	O 614
Grade	Light	Light	Brilliant	Brilliant	Dark	Dark
Polarization at 23° C.	92.50	90.55	87.85	90.00	85.55	85.00
Sucrose Clerget	92.48	90.50	88.06	90.19	85.96	85.47
Water	5.20	6.35	5.25	3.50	4.10	3.40
Impurities	2.32	3.15	6.69	6.31	9.94	11.13
Invert	1.32	1.96	3.23	2.99	5.02	5.52
Invert Per cent Impurities	56.9	62.2	48.3	47.4	50.5	49.6
(S — P)/I	—0.015	—0.026	+0.065	+0.063	+0.082	+0.085

TABLE IX—ANALYSIS OF A TABLE SIRUP MADE BY INVERSION OF CHAR-FILTERED LIQUOR

Brix	81.25
Polarization at 21.7° C.	7.10
Sucrose Clerget	22.86
Invert	55.87
(S — P)/I	0.282

TABLE X—ANALYSIS OF CHAR-FILTERED LIQUOR BEFORE AND AFTER ARTIFICIAL INVERSION, AND OF THE INVERTED LIQUOR AFTER BONE-BLACK TREATMENT

	Before Inversion	After Inversion	After Char Treatment
Brix	60.00	57.80	57.55
Dry Polarization at 21° C.	91.08	88.15	88.96
Dry Sucrose Clerget	91.20	88.82	89.49
Dry Invert	3.97	5.69	5.37
(Invert ÷ Sucrose) × 100	4.36	6.4	6.03
(S — P)/I	0.029	0.119	0.097

It has been shown that the action of bone-black is the chief cause of the decrease of (S—P)/I. Since bone-black absorbs invert from first material, where the decrease of (S—P)/I is most marked, it may be supposed that the reduction is due to a selective action of the char in removing more levulose than dextrose from the solution, although it must be borne in mind that this cannot be the only cause, since the last material, where increases of invert are shown, should also show increases of (S—P)/I, and the operation as a whole should show no change. To test this point, an artificial invert sugar solution at 60° Brix was treated with bone-black, and the proportions of dextrose and levulose before and after treatment were determined as well as might be by polarization at widely different temperatures. The results are shown in Table XI. The method of determining levulose by high-temperature polarization may not be accurate, but as both solutions were tested in exactly the same way, the results are at least comparable. The

TABLE XI—ANALYSIS OF A SOLUTION OF INVERT SUGAR BEFORE AND AFTER TREATMENT WITH BONE-BLACK

Tests made on an approximately 60 per cent solution of invert sugar made by inverting granulated sugar with HCl and neutralizing with NaOH.

86.45 g. solution to 100 cc., approximately 52 g. total sugar per 100 cc., or 40 per cent, 20 per cent each dextrose and levulose.

	Before Treatment	After Treatment
Reading ° V. at 20° C.	—63.10	—58.60
Reading ° V. at 87° C.	+ 0.20	+ 3.85
Change per ° C.	0.945	0.932
Levulose	30.6	30.2
Dextrose	30.1	31.0
Total Sugars	60.7	61.2
Levulose, Per cent Total Sugars	50.4	49.3
Dextrose, Per cent Total Sugars	49.6	50.7

$$\text{Levulose} = \frac{\text{Change per } ^\circ\text{C.} \times 100}{0.0357 \times 86.45}$$

$$\text{Rotation due to levulose} = \frac{\text{Per cent levulose} \times 93.30 \times 86.45}{66.5 \times 26}\ ^\circ\text{V.}$$

Rotation due to dextrose = Observed reading — Rotation due to levulose

$$\text{Per cent dextrose} = \text{Rotation due to dextrose} \times \frac{66.5 \times 26}{86.45 \times 53.08},$$

where + 66.5 = specific rotation of sucrose
+ 53.08 = specific rotation of dextrose at 20 per cent
— 93.30 = specific rotation of levulose at 20 per cent

polarizations at 87° C. and the calculated proportions of dextrose and levulose show clearly that the above assumption is correct and that char absorbs levulose from invert sugar more extensively than dextrose.

Another point which should be brought to the attention of sugar refiners is this: Since the value of (S — P)/I decreases greatly during refining, while the actual quantity of invert in products is about equal to that in the raw sugar, inversion balancing invert losses, it follows that losses of sucrose figured on Clerget tests will exceed those figured from polarizations. This fact has not been generally recognized. Although all refiners know that the polarization does not equal the true sucrose, it has been supposed that loss in polarization represents closely the loss in sucrose. Also, the final value of (S — P)/I seems to be about the same, regardless of the raw sugar used, so that statements based on polarization are particularly optimistic as regards sucrose losses when the raw sugars have high values for (S — P)/I. With regard to the removal of organic nonsugars during refining, the statements based on polarizations are also very deceptive. Since the organic is ordinarily taken as the difference between 100 and the sum of the percentages of the determined constituents, it is, of course, too high where polarizations are used. It is much more nearly correct, however, in the refined products than in the raw sugar. The true removal of organic, therefore, is not as great as appears when polarizations are used in the analyses.

In this paper two causes of the changes in the polarizing constants of sugar during refining have been indicated, the destruction of levulose by the action of heat and lime, and the absorption of levulose in excess of dextrose by bone-black. It has also been stated that a further explanation of the change during char filtration is required. Dr. Browne, in a letter to the writer, suggests that there are doubtless isomeric changes by which dextrose and levulose undergo molecular rearrangements into mannose and the so-called unfermentable sugars, glutose, etc. If this is the case the phenomenon should be related more specifically to the action of bone-black.

DICYANODIAMIDE: A RAPID, DIRECT METHOD FOR ITS DETERMINATION IN CYANAMID AND MIXED FERTILIZERS[1]

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In the course of an investigation upon the changes taking place in cyanamide when used in mixed fertilizers, it was found necessary to determine accurately the quantity of dicyanodiamide (cyanoguanidine) in various fertilizer mixtures and in samples of commercial calcium cyanamide (Cyanamid). The method previously used to determine dicyanodiamide is that of Caro,[2] as modified by Hager and Kern,[3] which consists in adding to the solution of dicyanodiamide a solution of silver nitrate and then an excess of sodium hydroxide, the latter throwing down a precipitate consisting of silver cyanamide (in case cyanamide is present), silver dicyanodiamide, and a large amount of silver oxide. The nitrogen in this precipitate is determined by the Kjeldahl method. A second portion of the solution is used for the determination of the cyanamide by the method of Perotti.[1] The difference in these two values represents the dicyanodiamide nitrogen. Kappen,[2] who later investigated these methods, showed that in the determination of dicyanodiamide in samples of Cyanamid containing urea, very large errors—sometimes as high as 50 per cent—occurred, due to the inclusion of urea in the precipitate. More recently, Hene and van Haaren[3] have modified the method by dissolving the precipitate first formed in nitric acid and reprecipitating with silver nitrate and sodium hydroxide. Using mixtures of pure cyanamide, dicyanodiamide, and urea, they have obtained fairly accurate results with the modified method. At best, however, the method is tedious, involving several precipitations and washings, and a final Kjeldahl determination on the product. It is moreover open to the objection that it is an indirect method, the dicyanodiamide being determined by difference, since all the nitrogen in the precipitate not deducted as cyanamide is considered to come from dicyanodiamide. Further modifications of this method were not attempted, as it was at once apparent that the method was fundamentally unsuited to the analysis of mixed fertilizers, since the presence of ammonium salts, which these fertilizers usually contain, would prevent the complete precipitation of the dicyanodiamide upon the addition of the sodium hydroxide.

It was desirable, therefore, to devise a direct and accurate means of determining dicyanodiamide, applicable to mixed fertilizers. A large number of compounds have been tried which it was hoped would give insoluble precipitates or colored solutions when added to dicyanodiamide solutions, and a method has been evolved which seems to be admirably suited to the purpose. The method depends upon the fact, observed by the author, that when a solution of silver picrate is added to a solution of dicyanodiamide, the latter is quantitatively precipitated as a double compound of silver picrate and dicyanodiamide, $C_6H_2(NO_2)_3OAg.C_2H_4N_4$. This new double compound we have named *silver picrate-mono-cyanoguanidine*. It forms in small crystals which quickly settle out of the solution and can be separated upon a Gooch crucible very rapidly, so that the analysis can be carried out in a very short time. Neither cyanamide nor urea give any precipitate when their solutions are treated with silver picrate, and have no effect upon the analysis for dicyanodiamide. The molecular weight of the compound is 420.22, five (4.991) times that of dicyanodiamide, a fact which greatly enhances the accuracy of the method, since an error of 1 mg. in the precipitate will mean an error of only 0.2 mg. of

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[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] *Z. angew. Chem.*, **23** (1910), 2405.

[3] *Ibid.*, **29** (1916), 309.

[1] *Rend. soc. chim. ital.*, **1904**, 192.

[2] *Z. angew. Chem*, **31** (1918), 29.

[3] *Ibid.*, **31** (1918), 129.

dicyanodiamide or 0.13+ mg. of nitrogen. While silver picrate-mono-cyanoguanidine is not insoluble in water, 100 cc. dissolving 0.12 g. of the compound at 25°, the presence of an excess of silver picrate, as used in the method, renders it practically insoluble. As shown below, this procedure reduces the solubility to 0.0044 g. in 100 cc. of the resulting solution, which corresponds to 0.0009 g. of dicyanodiamide. While for ordinary work this constant error is practically negligible, if greater accuracy is desired it is best to add to the weight of the precipitate 0.0044 g. for each 100 cc. of the solution from which it was filtered.

While it was shown that silver picrate is the causative agent in producing the double compound, the use of prepared silver picrate is not at all necessary, since the mixture of silver nitrate and picric acid gives the same reaction. In fact, the latter mixture serves even better, because the resulting solution is very slightly supersaturated in respect to silver picrate, a condition which could not be secured by adding to the dicyanodiamide solution a saturated solution of silver picrate. This supersaturation is not at all objectionable, since it was found that several days elapsed before any crystals of silver picrate appeared. Solid silver picrate, moreover, is probably explosive under certain conditions.

Two curious properties of silver picrate-mono-cyanoguanidine should prove useful in the qualitative test for dicyanodiamide. We refer to the formation of a gel, which quickly changes to crystals, when silver picrate is added to solutions of dicyanodiamide containing 0.5–4.0 mg. per cc., and, second, to the unusual form of the crystals of the compound when viewed under the microscope. Since the author was unable, either by searching through the literature or by experiments upon substances which might be present in the materials investigated, to find any compounds which possess anything like these two characteristics, it appears that positive results with these two tests would serve absolutely to confirm the presence of dicyanodiamide.

A second double compound of silver picrate and dicyanodiamide, *silver picrate-di-cyanoguanidine*, $C_6H_2(NO_2)_3OAg.2C_2H_4N_4$, was obtained by using dicyanodiamide in excess and recrystallizing the product from water. The existence of this compound is of interest in the method of analysis outlined, since solutions of dicyanodiamide more concentrated than 2 mg. per cc. give results which are too low, due no doubt to the formation of some silver picrate-di-cyanoguanidine. That the correct formulas have been assigned to these compounds is shown by the analyses, and also by the fact that the weight of yellow compound precipitated in the quantitative determination of dicyanodiamide always corresponds to the formula for silver picrate-mono-cyanoguanidine. Moreover, analogous addition compounds of dicyanodiamide have been prepared. Caro,[1] working with fairly strong solutions of dicyanodiamide synthesized three double salts with silver nitrate: $AgNO_3.C_2H_4N_4$, $AgNO_3.2C_2H_4N_4$, and $AgNO_3.3C_2H_4N_4$. Subsequently, Grossman and Schück[1] prepared $CuSO_4.2C_2H_4N_4.4H_2O$, $CdSO_4.C_2H_4N_4.2H_2O$, and $HgCl_2.C_2H_4N_4$.

EXPERIMENTAL PART

PURE DICYANODIAMIDE—Dicyanodiamide was prepared by the method of Hale and Vibrans,[2] which gave a good yield of large, transparent needles which melted exactly at 205° C.

SILVER PICRATE-MONO-CYANOGUANIDINE—To a solution of dicyanodiamide, containing 0.3 g. of the compound in 500 cc. of water, were added 75 cc. of a 5 per cent solution of silver nitrate and then 500 cc. of a saturated solution of picric acid. After about a minute the solution was vigorously stirred, which caused the appearance of a yellow crystalline precipitate. The mixture was allowed to stand for about 10 min., at the end of which time the precipitation was complete and the crystals had formed a layer on the bottom of the beaker. The precipitate was collected upon a filter, washed with a little water and then with a small amount of ether, and dried at 100° for 30 min. The crystals were of a bright yellow color, very slightly soluble in cold water but much more so in hot water, slightly soluble in alcohol and acetone, and practically insoluble in ether. When heated to 235°, they softened and turned brown, and a yellow solid collected on the cooler parts of the melting-point tube.

	N	Ag
Found	23.18	26.01
	23.10	
Calculated for $C_6H_2(NO_2)_3OAg.C_2H_4N_4$	23.34	25.67

A second experiment using a saturated solution of silver picrate instead of the mixture of silver nitrate and picric acid yielded a precipitate which was identical with the crystals described above.

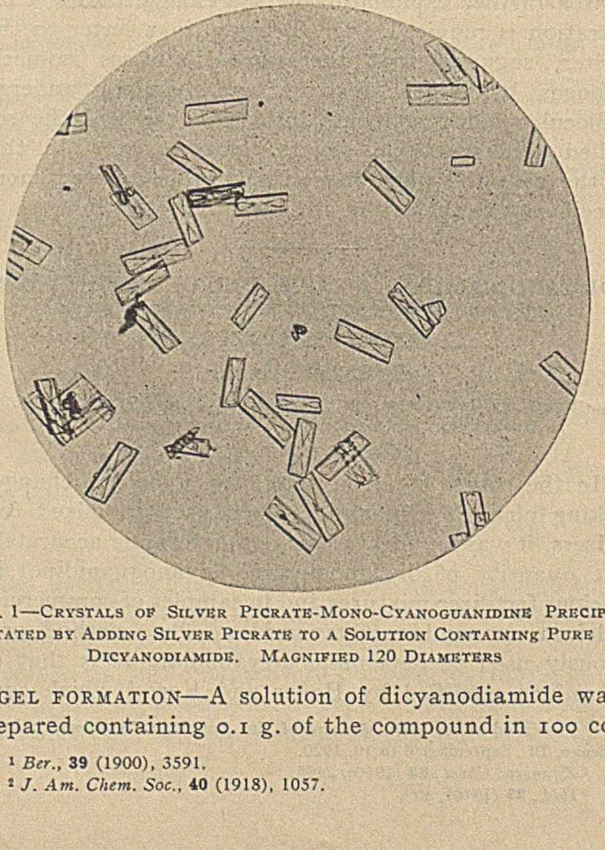

FIG. 1—CRYSTALS OF SILVER PICRATE-MONO-CYANOGUANIDINE PRECIPITATED BY ADDING SILVER PICRATE TO A SOLUTION CONTAINING PURE DICYANODIAMIDE. MAGNIFIED 120 DIAMETERS

GEL FORMATION—A solution of dicyanodiamide was prepared containing 0.1 g. of the compound in 100 cc.

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[1] *Loc. cit.*

[1] *Ber.*, **39** (1900), 3591.

[2] *J. Am. Chem. Soc.*, **40** (1918), 1057.

of water. The temperature of the solution was 20°. Fifteen cc. of 5 per cent silver nitrate were added and then 100 cc. of a saturated solution of picric acid, the latter solution also being at 20°. Almost at once the resulting solution set to a stiff jelly whose rigidity was so great that the beaker could be practically inverted without disturbing the gel. In about a minute, however, the gel began to liquefy at its edges, its mass contracting and leaving a layer of solvent between itself and the walls of the beaker. This contraction rapidly continued, and within 5 min. the gel had been entirely transformed to a crystalline precipitate which collected in a layer at the bottom of the beaker. When viewed under the microscope these crystals had the appearance shown in Fig. 1. It was found that the limits of concentration producing a good gel were from 0.6 to 4.0 mg. per cc.; solutions containing more than 4 mg. of dicyanodiamide per cc. giving a curdy precipitate. The disintegration of the gel was much retarded by employing a lower temperature, or by the presence of certain impurities found in some fertilizer mixtures, and for this reason it is advisable when analyzing mixed fertilizers to stir the solution two or three times during the first few minutes, thus avoiding the gel stage.

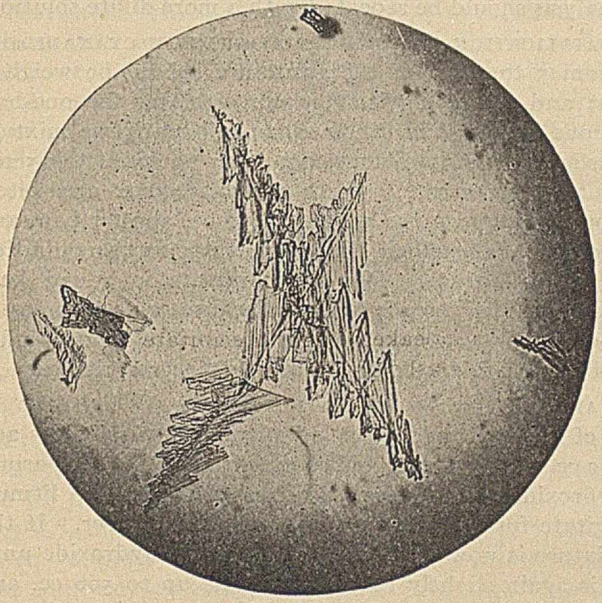

FIG. 2—CRYSTALS OF SILVER PICRATE-MONO-CYANOGUANIDINE PRECIPITATED IN THE PRESENCE OF FERTILIZER MATERIALS. MAGNIFIED 120 DIAMETERS

MICROSCOPIC APPEARANCE OF THE CRYSTALS—When silver picrate-mono-cyanoguanidine is formed as a gel and then allowed to crystallize, the crystals when viewed under the microscope (low power, magnification about 100 diameters) appear as in Fig. 1. They are almost perfect in form and appear to be very thin in one dimension. The exposed surface has the appearance of a slightly oblique parallelogram with four lines drawn from the four corners which meet at a point at the center. These lines are very distinct and seem to be the axes of the crystal since in imperfectly formed crystals they still persist. When the solution is stirred vigorously, causing direct precipitation of the crystals without passing through the gel stage, the resulting crystals are smaller but have the same general appearance as shown in Fig. 1, although considerable twinning is in evidence.

Certain compounds which are usually present when mixed fertilizers are analyzed cause a rather striking modification of the crystals.

Twelve grams of acid phosphate fertilizer were suspended in 100 cc. of water, and to this were added 100 cc. of a saturated solution of barium nitrate, and then a saturated solution of barium hydroxide, until the mixture was alkaline to litmus. This mixture was stirred for half an hour, made up to 500 cc., and filtered. Fifty cc. of this solution were made slightly acid with dilute nitric acid and treated with 5 cc. of a solution of dicyanodiamide (containing 21.0 mg.), 7 cc. of a 5 per cent silver nitrate solution, and 50 cc. of a saturated solution of picric acid. The beaker was left in an ice-water bath for 30 min., being stirred very gently once or twice during this period. Large crystals formed, a photomicrograph of which is shown in Fig. 2. An examination will show that the four lines shown in the crystals of Fig. 1 still persist, but that along two of the lines a great deal of twinning has taken place, resulting in these very striking "phantom crystals." The weight of the crystals was found to be 0.1054 g., corresponding to 21.1 mg. of dicyanodiamide, and this, together with their behavior when subjected to a melting-point determination, showed that they were identical with the crystals of Fig. 1.

A second experiment was carried out as above, except that 2 g. of ammonium sulfate were added to the acid phosphate, and the dicyanodiamide (0.2 g.) was added in the solid state, the mixture then being treated with water, barium nitrate, etc. These crystals, shown in Fig. 3,[1] were found to be identical with those already described.

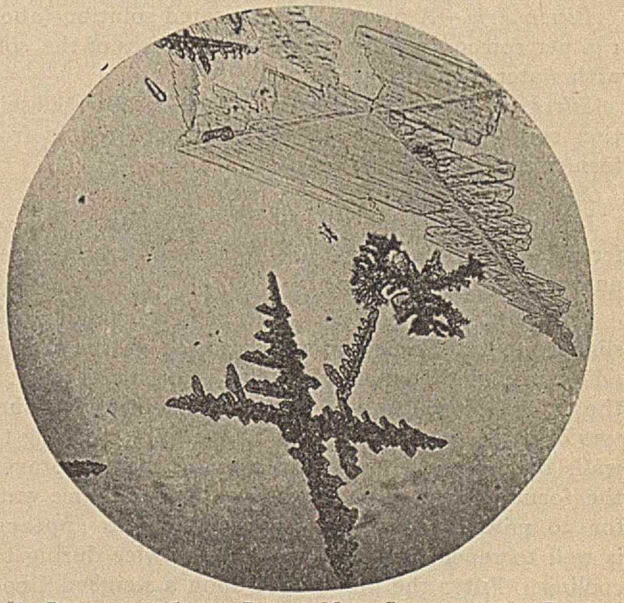

FIG. 3—CRYSTALS OF SILVER PICRATE-MONO-CYANOGUANIDINE PRECIPITATED IN THE PRESENCE OF FERTILIZER MATERIALS CONTAINING AMMONIUM SALTS. MAGNIFIED 120 DIAMETERS

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[1] The author is indebted to Mr. G. L. Keenan of the Microchemical Laboratory, Bureau of Chemistry, for making the above photomicrographs.

SOLUBILITY OF SILVER PICRATE-MONO-CYANOGUANIDINE IN WATER AND IN A SATURATED SOLUTION OF SILVER PICRATE—One hundred cc. of a saturated aqueous solution of the silver compound were evaporated to dryness in a weighed dish. To each of two other 100-cc. portions were added 15 cc. of 5 per cent silver nitrate solution and 100 cc. of saturated picric acid solution. The beakers containing the solutions were cooled in ice water for 30 min. with occasional stirring. The precipitates were collected on weighed Gooch crucibles, washed with a little saturated solution of silver picrate-mono-cyanoguanidine and with a little ether, dried for 30 min. at 100°, and weighed.

The following results were obtained:

Solubility of compound in 100 cc. of water	0.1128 g.
Compound precipitated by the silver picrate solution	0.1028 g.
Compound precipitated by the silver picrate solution	0.1037 g.
Quantity remaining in solution	0.0095 g.
Quantity remaining in 100 cc	0.0044 g.

SILVER PICRATE-DI-CYANOGUANIDINE—This compound was prepared by precipitating a saturated solution of dicyanodiamide with silver nitrate and picric acid, and recrystallizing the resulting product twice from water. It formed long, silky needles of a dark yellow color, the solubilities of which in various solvents very much resembled those of the corresponding mono-compound.

	N	Ag
Found	30.51	21.53
	30.43	
Calculated for $C_6H_2(NO_2)_3OAg.2C_2H_4N_4$	30.55	21.39

METHOD OF ANALYSIS

REAGENTS. *Silver Nitrate*—A 5 per cent solution.

Picric Acid—A practically saturated solution (about 1 g. per 100 cc.) made by shaking an excess of the solid with water for a minute or two.

Silver picrate-mono-cyanoguanidine—A saturated solution contained in a wash bottle. Precipitates from former analyses can be used.

Ether—Also contained in a wash bottle.

In addition to the above, the analysis of mixed fertilizers requires saturated solutions of barium nitrate and of barium hydroxide.

PROCEDURE—Make the solution of dicyanodiamide slightly acid to litmus. To each 100 cc. of this solution add 15 cc. of the silver nitrate solution and 100 cc. of the saturated solution of picric acid. Stir vigorously two or three times during the first 2 min., rubbing the walls of the beaker with the stirring rod, to prevent the formation of gel. Place the beaker in ice water for 30 min. In case crystals are slow to appear it is well to repeat the stirring once or twice during the cooling. Filter the precipitate upon a weighed Gooch crucible. The pad of asbestos should be very thin because the large crystals are not at all difficult to retain on the filter. With a properly prepared pad the mixture can be filtered almost as fast as it can be poured into the crucible. Wash out the crystals adhering to the walls of the beaker with the saturated solution in the wash bottle. It is sometimes necessary to employ a "policeman." Wash the precipitate once or twice with a little ether, dry in the oven 30 min. at 100°, cool in the desiccator, and weigh. To the weight of the precipitate add 0.0044 g. for each 100 cc. of the solution from which the crystals were filtered. The weight divided by five gives the quantity of dicyanodiamide in the solution analyzed. Should the analysis show that the original solution contained more than 2 mg. of dicyanodiamide per cc., which would give a precipitate of over 0.5 g. for each 100 cc. of solution filtered, the results are probably too low, and the analysis should be repeated with a more dilute solution.

APPLICATION TO COMMERCIAL CALCIUM CYANAMIDE—From 5 to 10 g. of the substance should be weighed out and agitated with 300 cc. of water for one-half to one hour. Add dilute nitric acid until the mixture is slightly acid to litmus, and then 75 cc. of the 5 per cent silver nitrate. Make up to 500 cc. and filter. For the analysis use a 100 or 200 cc. aliquot part and proceed as described above, omitting further addition of silver nitrate. The silver nitrate is added here before the mixture is filtered because some samples of Cyanamid contain sufficient carbides and similar substances to give a precipitate with silver nitrate.

APPLICATION TO MIXED FERTILIZER—Weigh out 20 g. of material, add 50 cc. of water, and stir. Now add 100 cc. of the solution of barium nitrate and then barium hydroxide until the mixture reacts alkaline to litmus. Agitate for 30 min., preferably with a stirrer. If the mixture is now acid, add more barium hydroxide until it is again slightly alkaline. Make up to 500 cc. and filter through a fluted filter. Use a 200-cc. portion for the analysis, proceeding as described above. If chlorides are present it will be necessary to filter again after the addition of the silver nitrate, before proceeding with the addition of the picric acid. In case the mixed fertilizer is unusually high in potassium salts, it is possible that the method will cause the precipitation of potassium picrate. Such an occurrence will be easily evident from the long needles thrown down, and also from the fact that the ether used to wash the precipitate will be colored a bright yellow. In this case a more dilute solution of the sample should be employed. The presence of cottonseed meal interferes with the analysis, certain soluble materials from the meal forming a gelatinous precipitate with the picric acid. This can be avoided by adding 30 cc. of a 10 per cent lead acetate solution immediately after the addition of barium hydroxide. If this is done, it is necessary to add more nitric acid when the solution is acidified, as the presence of acetates tends to lower the H^+-ion concentration, and if cyanamide is present it will be precipitated when the silver nitrate is added. If silver cyanamide should appear, it can be redissolved by adding more nitric acid and the analysis carried out as usual.

RESULTS OF ANALYSES BY THE METHOD

PURE DICYANODIAMIDE—Samples of this compound were weighed out and dissolved in varying volumes of water and the analysis carried out as described above. The results are given in Table I. The last example, where the cyanamide content of the solution analyzed was 3.33 mg. per cc., shows that with this concentration of dicyanodiamide the results are somewhat too low.

Table I

Volume of Dicyanodiamide Solution Cc.	Weight of Dicyanodiamide Used Mg.	Weight of Dicyanodiamide Found Mg.
50	50.0	49.9
100	50.0	49.3
100	50.0	49.8
50	34.4	35.5
100	50.0	49.2
50	56.3	56.4
25	2.5	2.3
50	50.0	49.4
25	50.0	48.9
30	100.0	93.6

DICYANODIAMIDE AND CYANAMIDE—To a solution containing 100 mg. of cyanamide ($CNNH_2$) in 50 cc. there were added 41.8 mg. of pure dicyanodiamide. Two such solutions were analyzed. The analysis gave 41.9 mg. and 42.2 mg. dicyanodiamide. Similar analyses carried out with the cyanamide solution alone showed no dicyanodiamide.

DICYANODIAMIDE AND UREA—A solution, containing 50 mg. of urea and 20 mg. of dicyanodiamide in 50 cc. of water gave on analysis 19.5 mg. of dicyanodiamide. A solution of pure urea containing 4 mg. per cc. gave no precipitate at all with the reagents, and the same result was secured with a urea solution containing 100 mg. per cc.

DICYANODIAMIDE AND MIXED FERTILIZER MATERIALS—A mixture was prepared consisting of acid phosphate (12 g.), ammonium sulfate (4.2 g.), potassium sulfate (1.5 g.), and dried peat (4 g.). To this were added 50 cc. of water containing 81.2 g. of dicyanodiamide. The mixture was treated with barium nitrate, barium hydroxide, etc., and the analysis carried out as described above for mixed fertilizers. The results of duplicate analyses were 81.5 and 81.5 mg. of dicyanodiamide.

A somewhat similar analysis has already been reported in one of the experiments under the heading of "microscopic appearance of the crystals."

THE CHANGES TAKING PLACE IN CYANAMID WHEN MIXED WITH FERTILIZER MATERIALS[1]

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In an attempt to analyze an aqueous extract of a mixed fertilizer for cyanamide by the method of Perotti,[2] it was found that the presence of phosphates interfered, since they, too, formed a precipitate with the silver nitrate upon making the solution alkaline with ammonium hydroxide. The difficulty was overcome by precipitating the phosphates by means of barium hydroxide and analyzing the filtrate. Although the manufacturer stated that the fertilizer contained considerable quantities of cyanamide, not even a trace was found. To test the accuracy of the method a mixed fertilizer was prepared containing a known weight of calcium cyanamide (Cyanamid) whose cyanamide content was known. The accurate results obtained upon analysis showed that the method was applicable. Some days later a second sample of this mixture was analyzed, and to our surprise it was found that all the cyanamide had disappeared. Another fertilizer mixture was now prepared, its composition being identical with the previous one, and at intervals over a period of two weeks samples were withdrawn and analyzed for cyanamide. The loss of cyanamide was very rapid, 60 per cent having disappeared in 24 hrs., and within 10 days it had practically all vanished. This at once suggested an investigation to determine, first, the cause of this rapid disappearance of cyanamide, and, second, the products resulting from the transformation.

A search through the literature showed that while a vast amount of work has been done in reference to the changes taking place when Cyanamid alone is added to the soil or is kept in storage, and that while studies have been made in regard to the changes occurring in the soluble phosphates of mixed fertilizer containing Cyanamid, it is a curious fact that no one seems to have paid any attention to the changes which may occur in cyanamide when this extremely reactive substance is mixed with other fertilizer materials. The present paper reports some results of such an investigation.

FACTORS CAUSING TRANSFORMATION OF CYANAMIDE

The fertilizer mixture which was prepared was composed of acid phosphate, ammonium sulfate, potassium sulfate, and Cyanamid (all being the usual commercial products), and dried peat. In order to ascertain which of these materials was instrumental in bringing about the rapid disappearance of cyanamide, mixtures containing Cyanamid and various combinations of these substances were prepared. Since it seemed probable that the acid phosphate was involved in the reaction it was used in each of the mixtures. The mixtures were: (1) acid phosphate and Cyanamid; (2) potassium sulfate, acid phosphate, and Cyanamid; (3) ammonium sulfate, acid phosphate, and Cyanamid; and (4) dried peat, acid phosphate, and Cyanamid. Samples from these mixtures were analyzed at intervals. While all of the mixtures caused a slight decrease in cyanamide, only Mixture 4 showed any considerable decrease, the rate here being rapid and practically parallel to that of the original mixture. This suggested that perhaps the dried peat was not so dry as the name would indicate, and an analysis of this material showed that it did contain 36 per cent of moisture. The other materials were practically dry, although the acid phosphate contained a little moisture. In a mixture containing acid phosphate, Cyanamid, and 8 per cent of water, the cyanamide decreased very rapidly, only 5 per cent of it remaining at the end of 3 days. Several similar mixtures exhibited this same rapid decrease in cyanamide content. To test the effect of moisture alone, moist quartz containing 10 per cent of water was mixed with Cyanamid. Here, too, there was a decrease in cyanamide, resulting finally in its disappearance, but the rate was by no means so rapid as when moist acid phosphate was employed, the loss of cyanamide in the latter mixture during the first day being eight times as great as that in the moist quartz mixture. On the other hand,

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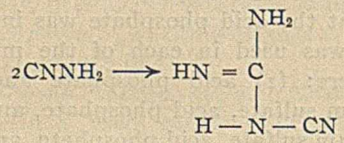
[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] *Rend. soc. chim. ital.*, **1904**, 192.

Cyanamid when mixed with practically dry acid phosphate remained unchanged even after 2 or 3 mo. This rapid disappearance of cyanamide must therefore be caused by the presence of acid phosphate and a small amount of moisture. This conclusion was further confirmed by experiments with complete mixed fertilizer, since only those samples in which these conditions existed (*i. e.*, acid phosphate and 5 to 10 per cent of moisture) showed any considerable decrease in cyanamide.

CHEMICAL CHANGES INVOLVED

Upon complete evaporation of a sample from one of the mixed fertilizers, the cyanamide of which had entirely disappeared, there was left a quantity of long needles, which were identified as dicyanodiamide by the method described in the preceding paper. A quantitative determination of dicyanodiamide, made upon another sample of this fertilizer, showed that 90 per cent of the cyanamide originally present had been transformed into dicyanodiamide. The mixture had now stood 30 days. At the end of 100 days it was again analyzed, and the results showed that the dicyanodiamide content was practically unchanged. Another mixture of Cyanamid and acid phosphate, containing about 10 per cent of moisture, was next prepared, and the changes taking place in cyanamide and dicyanodiamide content were followed by making simultaneous analyses for these two substances at intervals. Since the chemical change occurring in the formation of dicyanodiamide from cyanamide is simply the union of two molecules of cyanamide to form a molecule of dicyanodiamide, according to the equation



$$2\mathrm{CNNH_2} \longrightarrow \mathrm{HN} = \overset{\displaystyle \mathrm{NH_2}}{\underset{\displaystyle \mathrm{H-N-CN}}{\mathrm{C}}}$$

there is no alteration in weight, and if this reaction is the only one involved the weight of dicyanodiamide produced should equal that of the cyanamide lost; or, stated differently, the combined weights of cyanamide and dicyanodiamide should remain constant. This study served to confirm what was apparent from the results already secured: namely, that in the disappearance of cyanamide the principal chemical change was the formation of dicyanodiamide, and that under the conditions employed this was at all times practically quantitative. A similar study conducted with two complete mixed fertilizers yielded practically the same results, although toward the end of the period the amount of dicyanodiamide in the mixture did not so closely approximate the quantity of cyanamide which had disappeared, the final yield of dicyanodiamide representing only about 65 per cent of the loss in cyanamide. Whether this result was due to a parallel reaction which produced some other compound from the cyanamide—possibly urea—or whether part of the dicyanodiamide formed was subsequently decomposed into other compounds, has not yet been determined.

When Cyanamid and moist acid phosphate (6 to 10 per cent H_2O) were mixed, with or without other fertilizer materials, a rise in temperature of 20° to 30° C. was always observed, and the mixture set to a hard mass upon standing. When analyzed immediately there was no loss of cyanamide. The acid phosphate possessed but slight acidity, 10 g. of this material requiring 27.5 cc. of 0.1 *N* alkali to titrate to the neutral point with methyl red; yet when 1 g. of Cyanamid, which required 169 cc. of 0.1 *N* sulfuric acid to reach the same end-point, was added to 10 g. of moist acid phosphate, the resulting mixture, when added to water, was always acid to litmus. An alkaline mixture could be obtained only by adding a considerably larger quantity of Cyanamid. This can only mean an interaction between the acid phosphate and Cyanamid. de Nolinari and Ligot[1] and later Brackett[2] showed that when Cyanamid and acid phosphate were mixed there resulted a "reversion" of the phosphate, *i. e.*, the introduction of more calcium into the acid phosphate molecule to form insoluble phosphates. When these facts are considered together, they indicate the probable course of the reaction which results in the rapid loss of cyanamide. The calcium cyanamide and acid phosphate first react to form dicalcium or tricalcium phosphate and free cyanamide:

$$2\mathrm{Ca{:}NCN} + \mathrm{CaH_4(PO_4)_2} \longrightarrow 2\mathrm{CaHPO_4} + \mathrm{CNNH_2}$$

$$\mathrm{Ca{:}NCN} + 2\mathrm{CaHPO_4} \longrightarrow \mathrm{Ca_3(PO_4)_2} + \mathrm{CNNH_2}$$

and the free cyanamide thus produced is rapidly transformed into dicyanodiamide and other products.

Up to this point in the investigation, the fertilizer mixtures contained less than 1 part of Cyanamid to 10 parts of acid phosphate. In a mixture of moist acid phosphate and Cyanamid, containing 25 per cent of Cyanamid, there was also a rapid conversion to dicyanodiamide (practically quantitative), but only about 60 per cent of the cyanamide was thus transformed, and after this point was reached very little further change resulted. It is evident, therefore, that there is a limit to the quantity of cyanamide which a given quantity of moist acid phosphate will transform.

Reference has already been made to the fact that the mixing of Cyanamid with moist quartz caused a disappearance of cyanamide. It was found that most of the cyanamide was changed into dicyanodiamide. That this change would take place was somewhat to be expected, since Perotti[3] and Hager and Kern[4] have shown that when Cyanamid containing moisture was stored for several months a large portion of the cyanamide was converted into dicyanodiamide.

Finally, analyses were made of six samples of mixed fertilizer, containing varying amounts of Cyanamid, which had been prepared for certain 1920 field tests carried out by the Division.[5] Four weeks had elapsed since the fertilizers had been mixed. Each sample was found to contain a large quantity of dicyanodiamide, the

[1] *J. soc. agr. Brabant et Hainant*, **54** (1909), 161.

[2] THIS JOURNAL, **5** (1913), 933.

[3] *Atti acad. Lincei*, [5] **15** (1906), I, 48.

[4] *Z. angew. Chem.*, **29** (1916), 221.

[5] Prepared for field tests in experimental work being conducted by Dr. O. Schreiner, Dr. J. J. Skinner, and Mr. B. E. Brown, of Soil Fertility Investigations. The mixtures were prepared according to the usual fertilizer practice, no modifications being introduced, with a view of studying any changes in the cyanamide content.

amounts of this compound ranging from 11.4 to 33.4 lbs. per ton of the fertilizer mixtures.

EXPERIMENTAL DETAILS

MATERIALS EMPLOYED. *Acid Phosphate*—This was the usual type of fertilizer material, containing 16 per cent of available P_2O_5.

Ammonium Sulfate—The crude material of commerce, containing 25 per cent of NH_3.

Potassium Sulfate—The salt commonly used in fertilizer, containing 50 per cent of K_2O.

Cyanamid—This was technical calcium cyanamide, a hydrated material which was about a year old and contained 21 per cent of cyanamide and 2.3 per cent of dicyanodiamide. In two of the experiments, there was used a more recently purchased hydrated Cyanamid which contained 29.4 per cent of cyanamide and no dicyanodiamide.

METHODS OF ANALYSIS—A 20 g. sample (in mixtures containing more than 6 per cent of Cyanamid, a 10 g. sample was used) of the fertilizer mixture was stirred with 50 cc. of water. To this were added 100 cc. of a saturated solution of barium nitrate and then a solution of barium hydroxide until the mixture was slightly alkaline to litmus. The barium hydroxide was added to precipitate phosphates, but when ammonium sulfate was present this would have produced large amounts of ammonium hydroxide, which would convert some of the cyanamide to dicyanodiamide. The barium nitrate was therefore added to prevent this ammonia formation. The mixture was agitated vigorously for 30 min. with a mechanical stirrer, then transferred to a 500 cc. graduated flask, made up to the mark, thoroughly mixed, and filtered. Two 200 cc. portions were measured out, and one was analyzed for cyanamide and the other for dicyanodiamide. To determine cyanamide the method of Perotti, as modified by Brioux,[1] was employed, the precipitate of silver cyanamide being dissolved in dilute nitric acid and titrated against 0.1 *N* ammonium thiocyanate solution. For the determination of dicyanodiamide the method described in the preceding paper was used.

CHANGES IN CYANAMIDE CONTENT OF A MIXED FERTILIZER

Fertilizer Mixture A contained:

	Grams
Acid phosphate	100
Potassium sulfate	12
Ammonium sulfate	42
Cyanamid	10
Dried peat	36
TOTAL	200

The materials were ground together in a mortar until they would pass through a 20-mesh sieve, and further mixed on a large piece of glazed paper. The mixture was analyzed immediately for cyanamide, and the analysis was repeated at intervals for 13 days, with the results given in Table I and shown graphically in Fig. 1.

TABLE I—CHANGES IN CYANAMIDE CONTENT OF A COMPLETE MIXED FERTILIZER (MIXTURE A)

TIME Days	Mg. Cyanamide per G. Cyanamid Used
Immediately after mixing	220.0
1	95.5
3	75.6
4	46.2
6	41.1
13	23.1

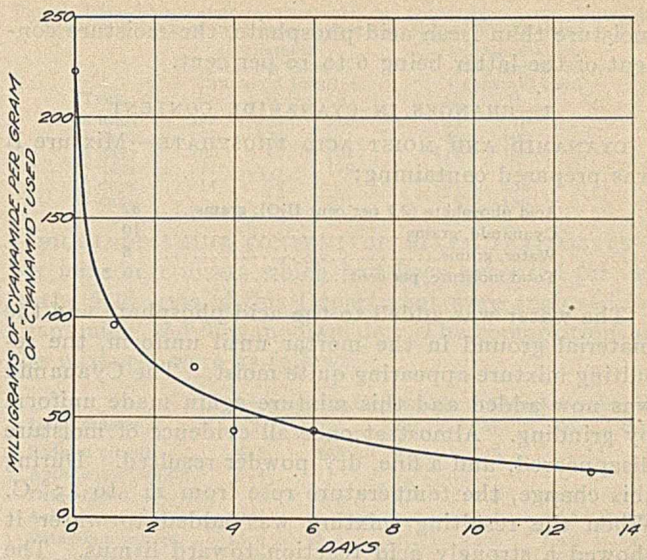


FIG. 1—CHANGES IN CYANAMIDE CONTENT OF A COMPLETE MIXED FERTILIZER CONTAINING "CYANAMID"

INFLUENCE OF VARIOUS FERTILIZER INGREDIENTS

Four mixtures were prepared containing various combinations of Cyanamid with the other materials used in the previous experiments, as follows:

(*a*)

	Grams
Acid phosphate	90
Cyanamid	10

(*b*)

	Grams
Acid phosphate	45
Ammonium sulfate	18
Cyanamid	5.5

(*c*)

Acid phosphate	45
Potassium sulfate	6
Cyanamid	5

(*d*)

Acid phosphate	45
Dried peat	18
Cyanamid	5.5

The results of analyses are given in Table II.

TABLE II—CHANGES IN CYANAMIDE CONTENT OF VARIOUS MIXTURES OF "CYANAMID" AND ACID PHOSPHATE WITH OTHER FERTILIZER MATERIALS

TIME Days	Mg. Cyanamide per G. Cyanamid Used (*a*)	(*b*)	(*c*)	(*d*)
Immediately after mixing	202	196	210	201
1	180	152	192	...
2	164	...	...	94
4	...	...	...	82
5	...	139	...	...
9	120	...	190	...

EFFECT OF MOISTURE CONTENT OF FERTILIZER MATERIALS

Moisture in the materials was determined by drying for 20 hrs. at 100° C.

	H_2O Per cent
Ammonium sulfate	0.4
Potassium sulfate	0.18
Dried peat	36.0
Acid phosphate	2.7

In the experiments described above the acid phosphate probably contained slightly more than 2.7 per cent of moisture since some weeks elapsed before the moisture content was determined, and during this time it had been stored in a paper bag exposed to the drying action of the air. At the time the experiments were performed the acid phosphate had already been considerably air-dried, so it contained much less

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[1] *Ann. chim. anal.*, **15** (1910), 341.

moisture than fresh acid phosphate, the moisture content of the latter being 6 to 10 per cent.

I—CHANGES IN CYANAMIDE CONTENT

CYANAMID AND MOIST ACID PHOSPHATE—Mixture B was prepared containing:

Acid phosphate (2.7 per cent H_2O), grams	82
Cyanamid, grams	10
Water, grams	8
Total moisture, per cent	10.2

The water was added to the acid phosphate and the material ground in the mortar until uniform, the resulting mixture appearing quite moist. The Cyanamid was now added and this mixture again made uniform by grinding. Almost at once all evidence of moisture disappeared, and a fine, dry powder resulted. During this change, the temperature rose from 24° to 45° C. When the resulting mixture was added to water it showed a strongly acid reaction toward litmus. The mixture was analyzed for cyanamide immediately and at intervals over a period of 6 days, the results being given in Table III.

TABLE III—CHANGES IN CYANAMIDE CONTENT OF A MIXTURE OF "CYANAMID" AND MOIST ACID PHOSPHATE (MIXTURE B)

TIME	Mg. of Cyanamide per G. of Cyanamid Used
0 hrs.	210
5 hrs.	97.6
2 days	21.4
6 days	17.3

CYANAMID AND AIR-DRY ACID PHOSPHATE—Mixture C contained:

Acid phosphate (2.7 per cent H_2O), grams	90
Cyanamid, grams	10
Total moisture, per cent	2.2

and was mixed as in the preceding experiment. Immediately after mixing it contained 223 mg. of cyanamide per gram of Cyanamid, and after standing 18 days it was found to contain 194 mg. per gram of Cyanamid used.

CYANAMID AND MOIST QUARTZ—A mixture, D, containing

Quartz (ground to 200 mesh), grams	90
Water, grams	10
Cyanamid, grams	11.1
Total moisture, per cent	9

was prepared and analyzed as in the previous experiments. There was no rise in temperature when the mixture was prepared, and it remained moist, clinging together like moist sand when the jar containing it was rotated. After a day an odor of ammonia was given off. At the end of 2 wks. it was somewhat more dry, but the particles still clung together, and it was by no means the dry powder described in the experiment with moist acid phosphate. Table IV gives the results of analyses of this material.

TABLE IV—CHANGES IN CYANAMIDE CONTENT OF A MIXTURE OF "CYANAMID" AND MOIST QUARTZ (MIXTURE D)

TIME	Mg. of Cyanamide per G. of Cyanamid Used
0 hrs.	213.6
24 hrs.	185.8
2 days	131.25
9 days	31.5

The results for Mixtures B, C, and D are shown graphically in Fig. 2.

AVAILABLE ACID IN ACID PHOSPHATE—One gram of acid phosphate was extracted for 0.5 hr. with 500 cc. of water. The filtrate was strongly acid to litmus. Upon titration against 0.1 *N* sodium hydroxide, using methyl red as an indicator, 2.75 cc. of the alkali were required.

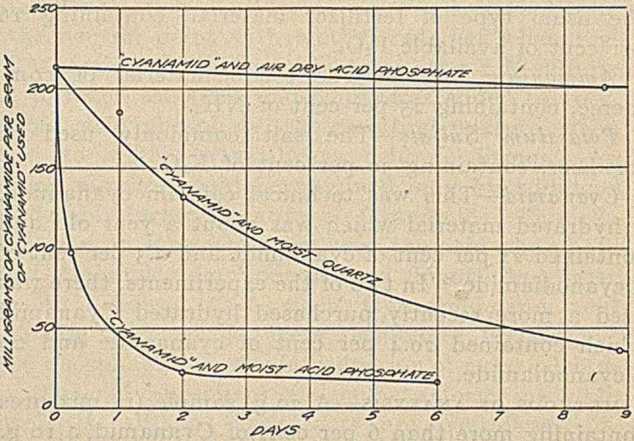

FIG. 2—CHANGES IN CYANAMIDE CONTENT OF "CYANAMID" WHEN MIXED WITH AIR-DRY ACID PHOSPHATE, MOIST ACID PHOSPHATE, AND MOIST QUARTZ

AVAILABLE ALKALI IN CYANAMID—One gram of the Cyanamid was stirred vigorously with 500 cc. of water for 30 min., and filtered. The filtrate, which was strongly alkaline to litmus, required 169 cc. of 0.1 *N* sulfuric acid for neutralization with methyl red as indicator.

DICYANODIAMIDE CONTENT OF THE MIXTURES—Twenty grams of Mixture B were stirred for 30 min. with 200 cc. of absolute acetone, and filtered. The acetone extract was evaporated to dryness, leaving a quantity of long needles mixed with some dark material. Recrystallization of the residue from water gave colorless needles, melting at 205°, whose melting point was unchanged when mixed with dicyanodiamide. A solution of these crystals gave yellow crystals of silver picrate monocyanoguanidine (m. p. 230°) upon treatment with picric acid and silver nitrate (Fig. 1, preceding paper). A quantitative determination of dicyanodiamide in Mixture B gave 179 mg. of dicyanodiamide per gram of Cyanamid, at the end of 4 wks. At the end of 15 wks., the mixture contained 193.5 mg. of dicyanodiamide per gram of Cyanamid used. Mixture C contained but 7.9 mg. of dicyanodiamide per gram of Cyanamid. Mixture D at the end of 9 days contained 171.2 mg. of dicyanodiamide per gram of Cyanamid used. A quantitative conversion of the cyanamide to dicyanodiamide would have required the appearance of 230 mg. of dicyanodiamide per gram of Cyanamid used.

II—SIMULTANEOUS CHANGES IN CYANAMIDE AND DICYANODIAMIDE CONTENT

CYANAMID AND MOIST ACID PHOSPHATE—The following Mixture E was prepared:

Acid phosphate (2.7 per cent H_2O), grams	184
Water, grams	16
Cyanamid, grams	22.2
Total moisture per cent	10.2

Analyses for cyanamide and dicyanodiamide were made immediately, and at intervals over a period of 8 days. The results are shown in Table V and Fig. 3.

Table V—Simultaneous Changes in Cyanamide and Dicyanodiamide in a Mixture of "Cyanamid" and Moist Acid Phosphate (Mixture E)

Time	Cyanamide (Mg. per G. of Cyanamid Used)	Dicyanodiamide (Mg. per G. of Cyanamid Used)
0 hrs.	208.9	13.5
5 hrs.	130.0	113.2
28 hrs.	75.6	175.8
2 days	49.8	184.6
5 days	44.6	180.2
8 days	30.5	182.4

The above experiment was twice repeated with practically identical results.

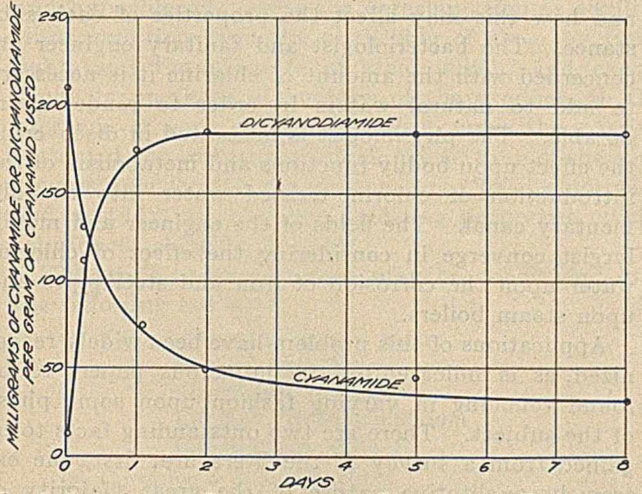

Fig. 3—Simultaneous Disappearance of Cyanamide and Formation of Dicyanodiamide in a Mixture of "Cyanamid" and Acid Phosphate

MOIST ACID PHOSPHATE AND EXCESS OF CYANAMID—Mixture F was prepared and studied in the usual way. The Cyanamid used was the more recently purchased sample containing 29.4 per cent of cyanamide. This mixture, when added to water, was alkaline to litmus.

Acid phosphate (2.7 per cent H_2O), grams	67
Water, grams	8
Cyanamid, grams	25
Total moisture, per cent	9.8

Table VI gives the results.

Table VI—Simultaneous Changes in Cyanamide and Dicyanodiamide in a Mixture of Moist Acid Phosphate and an Excess of "Cyanamid" (Mixture F)

Time	Cyanamide (Mg. per G. of Cyanamid Used)	Dicyanodiamide (Mg. per G. of Cyanamid Used)
0 hrs.	277	0
2 days	191	97
8 days	155	122
41 days	127	142

CYANAMID IN COMPLETE FERTILIZER MIXTURES—Three complete fertilizer mixtures were prepared, their composition being:

	(Mixtures G and H)	(Mixture I)
Acid phosphate (2.7 per cent H_2O), grams	200	200
Potassium sulfate, grams	24	24
Ammonium sulfate, grams	84	84
Dried peat (9 per cent H_2O), grams	42	72
Water, grams	30	..
Cyanamid, grams	20	20
Total moisture, per cent	9.8	3.2

Mixtures G and I were prepared by grinding in the mortar. Since in actual fertilizer practice the materials are merely mixed with a shovel, Mixture H was mixed by means of a spatula. The results are given in Table VII.

Table VII—Simultaneous Changes in Cyanamide and Dicyanodiamide Content of Three Complete Mixed Fertilizers

Time	Cyanamide (Mg. per G. of Cyanamid Used) G	H	I	Dicyanodiamide (Mg. per G. of Cyanamid Used) G	H	I
0 hrs.	223	221	210	14	10	...
1 day	143	128	...	86	100	...
3 days	102	67	201	111	126	...
15 days	...	...	199	...	...	...
18 days	14	9	...	104	136	...
34 days	...	5	201	98	136	...

DICYANODIAMIDE CONTENT OF MIXED FERTILIZERS—Six mixed fertilizers which had been prepared for use in the field tests of this Department were analyzed for cyanamide and dicyanodiamide. The compositions of the mixtures were as follows:

Ingredients	Mixture, Weight in Pounds (1)	(2)	(3)	(4)	(5)	(6)
Sodium nitrate	4.5	4.5	6.8	2.3	..	..
Ammonium sulfate	3.4	..	..	..	..	4
Dried blood	..	5.3	8.4	2.7	10.7	..
Acid phosphate	42.7	42.7	42.7	42.7	42.7	25
Potassium sulfate	13.6	13.6	13.6	13.6	13.6	4
Cyanamid	7.8	7.8	3.9	7.8	7.8	8
Sand (air-dry)	25.7	25.8	22.3	22.9	22.9	9
Total	97.7	99.7	97.7	97.6	97.7	50

The Cyanamid used in the first five mixtures was 2 yrs. old and contained 15.4 per cent of cyanamide and 6.2 per cent of dicyanodiamide. For Mixture 6 there was used the more recently purchased Cyanamid containing 29.4 per cent of cyanamide. The results are given in Table VIII.

Table VIII—Cyanamide and Dicyanodiamide Content of 20 Grams of Complete Fertilizer Mixtures when Mixed and Five Weeks Afterward

Mixture	Cyanamide Added Mg.	Cyanamide Found after 5 Wks. Mg.	Dicyanodiamide Added Mg.	Dicyanodiamide Found after 5 Wks. Mg.
1	240	89	99	214
2	240	106	99	211
3	120	40	50	114
4	320	171	132	249
5	240	142	99	201
6	940	648	...	334

EFFECT OF USING SMALLER PROPORTIONS OF CYANAMID—Four mixtures of moist acid phosphate and Cyanamid were prepared, containing in each 1000 g. of mixture 25, 50, 75, and 100 g., respectively, of Cyanamid. Since mixed fertilizers commonly contain about 50 per cent of acid phosphate, these mixtures would correspond to 25, 50, 75, and 100 lbs. of Cyanamid per ton of mixed fertilizer. They were prepared as in the previous experiments, using another supply of acid phosphate containing 3 per cent of moisture, to which was added water so that all mixtures contained practically 10 per cent of moisture, to approximate the moisture condition of commercial acid phosphate. In the three lower concentrations of Cyanamid duplicate mixtures were prepared, using for comparison the acid phosphate employed in the previous experiments.

After 3 days the mixtures were analyzed for cyanamide and dicyanodiamide, with the results given in Table IX.

Table IX—Changes Taking Place in 20 Grams of Mixtures of Moist Acid Phosphate with Varying Amounts of "Cyanamid"

Parts Cyanamid in 1000 Parts Mixture	When Mixed Cyanamide Mg.	After 3 Days Cyanamide Mg.	After 3 Days Dicyanodiamide Mg.
25	145	99	6
25	145	29	7
50	290	97	91
50	290	85	74
50	290	66	125
75	435	61	348
75	435	44	353
100	580	32	498

It will be noticed that while the formation of dicyanodiamide is less with the smaller quantities of Cyanamid used in the fertilizer, yet the change to dicyanodiamide is still very considerable with 50 lbs. per ton.

CONCLUSIONS

Further investigations are being conducted, but the results already secured seem to warrant the following conclusions, at least in so far as the conditions of concentration, temperature, and moisture here reported on are concerned:

1—When Cyanamid is mixed with fertilizer materials containing acid phosphate and 5 to 10 per cent of moisture, the cyanamide content decreases with great rapidity.

2—This change is represented partially by, and in the higher concentrations principally by, the formation of dicyanodiamide.

3—A given quantity of moist acid phosphate is able to transform a limited amount of calcium cyanamide.

4—Cyanamid is not affected by dry acid phosphate.

5—Moisture alone is able to cause the conversion of cyanamide to dicyanodiamide, but the change is much slower than when acid phosphate is present.

Since it has been repeatedly shown that dicyanodiamide is valueless as a fertilizer material, and, moreover, is toxic to many plants,[1] the formation of this compound in fertilizer materials seems undesirable. On first thought, it would appear that this conversion of cyanamide into dicyanodiamide could be avoided by employing dry fertilizer mixtures, but this overlooks the fact that when such mixtures are added to the soil, moisture conditions are at once provided, and the transformation may possibly then take place. Preliminary experiments carried out in this laboratory indicate that, under certain conditions at least, this is the case.

It should be noted that these unfortunate reactions between acid phosphate and Cyanamid do not in any sense imply that Cyanamid cannot be successfully used when mixed with other forms of phosphate. In this connection it should be noted that the Fixed Nitrogen Research Laboratory of the Ordnance Department has called our attention to the fact that lime nitrogen (Cyanamid) can be mixed with calcined and basic phosphates without the excessive production of dicyanodiamide noted when moist acid phosphate is used.

STUDIES ON THE CORROSIVE ACTION OF CHLORINE-TREATED WATER. I—THE EFFECTS OF STEEL ON THE EQUILIBRIUM: $Cl_2 + H_2O \rightleftharpoons HCl + HClO$, AND OF PRODUCTS OF THE EQUILIBRIUM ON STEEL

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In the entire range of the subject matter of chemistry there is scarcely a phase upon which more work has been done, and concerning which there is greater deviation of opinion expressed in the literature, than upon solutions of chlorine gas in water. The importance of a thorough knowledge of such solutions lies in the fact that so many distinct fields are concerned. The physical chemist is interested in all phases of the equilibrium established between the products of the reaction

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

and how this may affect the properties of each substance. The bacteriologist and sanitary engineer are concerned with the amount of chlorine it is necessary to add to natural waters in order to render them potable. The physiologist is interested in discovering the effect upon bodily functions and metabolism of the introduction of chlorine-treated water into the alimentary canal. The fields of the engineer and metallurgist converge in considering the effect of chlorine water upon the corrosion of iron and steel pipes and upon steam boilers.

Applications of this problem have been widely recognized, as is indicated by the numerous papers to be found touching in varying fashion upon some phase of the subject. There are two outstanding facts to be gained from a survey of the literature: first, the extremely qualitative nature of the great majority of these reported observations; and hence, second, the wide differences of opinion, even to the point of diametrical opposition, on some of the most fundamental points of the chemistry, corrosive effects, and physiological action. It is not within the scope of this paper to undertake any extensive critique of the work which has been done; the work which may be considered most authoritative will be referred to later. With these large discrepancies and rather serious omissions in the present knowledge of the solution of chlorine in water clearly in mind, this series of researches has been undertaken with the ostensible purpose of attempting to bring order out of an indefinite and unsatisfactory state of a scientific subject, with especial reference to the application to the city water supply of Nashville, Tennessee.

Of course, of the greatest importance from any standpoint is the question whether or not city water which has been treated with chlorine is physiologically injurious when used for drinking purposes. There is not to be found in the literature a record of any complete biological research of this kind, though work upon the effect of chlorine gas in respiratory processes is extensive and conclusive since the war. There is an almost even division of opinion among medical men as to whether chlorine-treated water is, or is not, injurious in metabolism. One writer finds it beneficial in the treatment of such diseases as infantile diarrhea, and another argues that even very slight traces are injurious to the organism. There must be established, therefore, by careful research upon living organisms just what the effect of chlorine-treated water is, and what the maximum allowable concentration of the gas may be without serious consequences.

Before any adequate interpretation of such experiments can be made, however, it is necessary to know

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[1] Brioux, *Ann. Sci. Agron.*, [3] **1** (1910), 241; Hovermann and Koch, *J. Landw.*, **64** (1916), 317; Pfeiffer and Simmermacher, *Landw. Vers.-Sta.*, **90** (1917), 415; Johnson, *Tid. Kemi, Farm. Terapi*, **15** (1918), 349; Cowie, *J. Agr. Sci.*, **9** (1919), 113.

exactly the chemistry involved—the compounds formed, and their concentration, activity, and relation to each other, when chlorine is dissolved in water. This paper is, therefore, preliminary to more practical work on the corrosive action upon living organisms and upon metal containers and pipes,[1] the cause and nature of which may then be adequately and scientifically explained. It involves essentially a study of the reaction between chlorine and water to form hydrochloric and hypochlorous acids; the determination of equilibrium conditions and the disturbing of them by time, light, and the presence of steel, alkali, and excess products; methods of analysis of the products in the presence of each other; the effect upon the passive state and the corrosion of steel; the settling of the controversy concerning the existence of "fixed chlorine;" and a study of some new oxidizing properties of the solution of chlorine in water.

The work to be described may be subdivided into the following heads:

- (*a*) The solution of chlorine in water:
    - Methods of analysis
    - Equilibrium in the system
    - Effect of iron on equilibrium
    - Interpretation of results
- (*b*) Corrosion of iron and steel:
    - Nature, and extent
    - Interpretation
    - Secondary effects

THE SYSTEM Cl_2–H_2O–HOCl–HCl

It has been long known that when the reaction

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

takes place out of contact of light and in the cold, equilibrium is established. There is, however, very great disagreement as to the exact conditions and concentrations which determine the equilibrium, and the constant has never been determined. Much better known is the action of sunlight upon chlorine water, in which the following monomolecular reaction proceeds:

$$2HOCl \rightleftharpoons 2HCl + O_2$$

Also well known is the extensive work on the reaction comprising the Deacon process

$$2H_2O + 2Cl_2 \rightleftharpoons O_2 + 4HCl$$

which is carried out at high temperatures in the presence of bricks soaked with $CuCl_2$ as catalyst. The equilibrium constant is about 2.4 at 430°.

A fourth equilibrium is the following:

$$3H_2O + 3Cl_2 \rightleftharpoons HClO_3 + 5HCl$$

which has been fully investigated by Sands,[2] Foerster,[3] Luther and McDougall,[4] and Olson.[5] The latter determined an equilibrium constant of 4.3×10^{-7} at 364° Å., and also found that the effect of hastening to equilibrium with iron as catalyst was unsatisfactory.

ANALYTICAL METHODS

Perhaps the greatest difficulty in establishing definite relationships in the first of the four above equations, with which this entire series of studies is concerned, is to be found in a method of analysis by which it would be possible to determine chlorine, and both hypochlorous and hydrochloric acids, in the presence of each other. The usual method for thus determining chlorine and hypochlorous acid in the presence of each other takes hydrochloric acid into account not at all, and thus introduces large errors. The determination is based upon the following reactions:

$$HOCl + 2NaI \rightleftharpoons NaCl + NaOH + I_2$$
$$Cl_2 + 2NaI \rightleftharpoons 2NaCl + I_2$$

One mole of HOCl sets free one mole of I_2 and produces at the same time one mole of NaOH, while the chlorine simply sets free an equivalent amount of iodine. After neutralizing the alkali with an excess of hydrochloric acid and determining the iodine by titration with sodium thiosulfate, the excess of hydrochloric acid is titrated with standard alkali solution. The NaOH produced by the action of hypochlorous acid upon the iodide obviously requires half as much of, say, 0.01 *N* acid, for neutralization as is required of 0.01 *N* $Na_2S_2O_3$ solution to react with the iodine set free by the action of the hypochlorous acid. From this is calculated how much of the $Na_2S_2O_3$ is required for the free chlorine. It is clear, therefore, that this method depends entirely upon the fact that the standard acid added is the *only HCl* present, where in reality there is in addition an indefinite amount of HCl formed in the reaction $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$, which would neutralize some of the NaOH formed when NaI and HOCl react. This fallacy has not been pointed out before. It is impossible, therefore, by the use of one sample to determine Cl_2, HOCl, and HCl in the presence of each other. Most of the preliminary experimental work of this paper was concerned with various possible analytical devices, some of which may be briefly described as follows:

(1) DETERMINATION OF TOTAL ACIDITY BY USUAL METHOD—The difficulty in this method lies in the use of indicators in the presence of chlorine and hypochlorous acid.

Methyl orange, rosolic acid, and phenolphthalein were tried out in order to determine which would be best in the titration for total acidity. It was found that neither of the first two would produce any stable color in the presence of Cl_2 and HOCl, no matter how much base or acid was added. It was found that phenolphthalein would give a stable color and definite end-point, provided that at least 1 cc. was used. Furthermore, the end-point depended upon whether this relatively large amount was added drop by drop, or poured in as rapidly as possible, with best results seemingly from the latter method. As an illustration of the lack of exactness of this method, the following data are quoted on the number of cc. of 0.01 *N* NaOH required to neutralize successive 25 cc. portions of the same sample: 17.5, 19, 16.2, 15.5, 16.7. The

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[1] Lillie [*Science*, **50** (1919), 259] has shown that there are fortunately some close analogies between many of the properties of metal surfaces and living protoplasm.

[2] *Z. physik. Chem.*, **50** (1904), 465.

[3] *J. prakt. Chem.*, **63** (1901), 141.

[4] *Z. physik. Chem.*, **62** (1908), 199.

[5] *J. Am. Chem. Soc.*, **42** (1920), 896.

reactions between the indicator and chlorine and hypochlorous acid led to results, therefore, which were at once nonconcordant and doubtful, unless exactly the same method of titration was used throughout. Attention is directed to the fact that methyl orange cannot under any circumstance be used, though its use is advocated by such an authoritative text as Treadwell.[1]

(2) REMOVAL OF HYPOCHLOROUS ACID—Methods dependent upon the removal of HOCl were not successful because of the incompleteness of the reactions. For example, a solution was shaken up with pure mercury in order to test the reaction

$$2Hg + 2HOCl \rightleftharpoons HgO.HgCl_2 + H_2O.$$

The oxychloride $HgO.HgCl_2$ first formed is immediately decomposed by the HCl present, and $HgCl_2$ passes into solution, leaving a precipitate of yellow-brown HgO. Subsequent treatment with NaI and titration with $Na_2S_2O_3$ for the determination of chlorine gives highly discordant results. Exposure to strong sunlight in order to decompose HOCl, of course, throws no light upon the relationship between Cl_2 and HOCl since both disappear at a monomolecular rate. The reaction

$$Ag_2O + 2HOCl \rightleftharpoons 2AgCl + O_2$$

and the decomposition in the presence of cobalt nitrate solution, with oxidation of the cobalt to higher valence, were found entirely unsatisfactory as quantitative methods, since both chlorine and hydrochloric acid are also involved.

(3) REMOVAL OF CHLORINE—One of the most promising analytical methods seemed to be found in the removal of chlorine by bubbling air through the solution and collecting the gas in another vessel containing sodium iodide solution, the HOCl remaining behind. de Mallman[2] reports that experiments upon the elimination of chlorine by a current of air showed that free chlorine is totally removed in 5 min. from 50 to 100 cc. solution, and that hypochlorous acid in the small quantities present is little, if at all, affected by aëration. Unfortunately, no data were cited to prove this. These experiments and others to be found do not preclude the possibility, however, of large errors which might arise from difficulties in manipulation, the existence of "free" and "fixed" (possibly hydrated and inactive) chlorine, appreciable decomposition of hypochlorous acid with formation of chlorine, and a minimum concentration below which it is impossible to remove *any* chlorine from chlorine water even in 15 min. As a matter of fact, as will be fully shown, the present researches have met with all of these contingencies and it is therefore impossible to make use of this method alone in determining chlorine and hypochlorous and hydrochloric acids together. It was found possible by careful work to remove the difficulties in manipulation so that, as the following tables will show, it was repeatedly found that the sum of the *two titrations*, after air was bubbled through and the gas collected in a second solution of NaI, checked exactly the total amount of $Na_2S_2O_3$ required by the solution

TABLE I

	Expt.	A—Solution Alone (50 Cc.)						B—In Presence of Low-Carbon Steel[1]					
(1) HOCl		1	2	3	4	5	6	7	8	9	10	11	12
Time Elapsed, Hrs.	(*a*)	0	24	48	72	96	120	0	24	48	72	96	120
As_2O_3,[2] Cc.	(*b*)	42.50	41.00	40.00	40.00	40.00	40.00	42.50	18.50	0	0	0	0
HOCl, G. per liter	(*c*)	0.4460	0.4305	0.4200	0.4200	0.4200	0.4200	0.4460	0.1942	0	0	0	0
HOCl, Moles per liter	(*d*)	0.0085	0.0082	0.0080	0.0080	0.0080	0.0080	0.0085	0.0037	0	0	0	0
(2) Cl_2 and HCl													
$Na_2S_2O_3$ (Total), Cc.	(*e*)	47.50	46.50	46.00	46.00	46.00	46.00	47.50	26.50	8.50	2.50	0.00	0.00
$Na_2S_2O_3$(HOCl), Cc.	(*f*)	42.50	41.50	40.00	40.00	40.00	40.00	42.50	18.50	0.00	0.00	0.00	0.00
$Na_2S_2O_3(Cl_2)$, Cc.	(*g*)	5.0	5.5	6.0	6.0	6.0	6.0	5.0	8.0	8.5	2.5	0.0	0.0
Cl_2, G. per liter	(*h*)	0.00355	0.003905	0.004260	0.004260	0.004260	0.004260	0.00355	0.00568	0.006035	0.00178	0.00000	0.00000
Cl_2, Equiv. per liter	(*i*)	0.00010	0.00011	0.00012	0.00012	0.00012	0.00012	0.00010	0.00016	0.00017	0.00005	0.00000	0.00000
NaOH (Back titration), Cc.	(*j*)	24.00	24.50	23.00	23.00	23.00	23.00	24.00	39.50	55.00	60.00	62.00	62.00
NaOH (from HOCl + NaI), Cc.	(*k*)	21.25	20.50	20.00	20.00	20.00	20.00	21.25	9.25	0.00	0.00	0.00	0.00
NaOH (Total), Cc.	(*l*)	45.25	45.00	43.00	43.00	43.00	43.00	45.25	48.75	55.00	60.00	62.00	62.00
HCl (25 Cc. added), Cc.	(*m*)	20.25	20.00	18.00	18.00	18.00	18.00	20.25	23.75	30.00	35.00	37.00	37.00
HCl, G. per liter	(*n*)	0.148	0.140	0.126	0.126	0.126	0.126	0.148	0.1734	0.2190	0.2555	0.2701	0.2701
HCl, Moles per liter	(*o*)	0.004	0.004	0.0035	0.0035	0.0035	0.0035	0.004	0.00475	0.0060	0.0070	0.0074	0.0074
(3) Air Bubbling													
$Na_2S_2O_3$ (1st), Cc.	(*p*)	35.50	36.00	35.00	36.00	37.00	38.50	35.50	19.00	8.50	2.50	0.00	0.00
$Na_2S_2O_3$ (2nd), Cc.	(*q*)	12.00	10.50	11.00	10.00	9.00	7.50	12.00	7.00	0.00	0.00	0.00	0.00
$Na_2S_2O_3$ (Total), Cc.	(*r*)	47.50	46.50	46.00	46.00	46.00	46.00	47.50	26.00	8.50	2.50	0.00	0.00
$Na_2S_2O_3$ (Decomp. of HOCl), Cc.	(*s*)	7.0	6.0	5.0	4.0	3.0	1.5	7.0	0.0	0.0	0.0	0.0	0.0
Decomp. HOCl, Per cent	(*t*)	16.5	15.6	12.5	10.0	7.5	3.75	16.5	0.0	0.0	0.0	0.0	0.0
$Na_2S_2O_3$ (Free Cl_2), Cc.	(*u*)	5.0	5.5	6.0	6.0	6.0	6.0	5.0	7.0	0.0	0.0	0.0	0.0
NaOH (Back titration), Cc.	(*v*)	24.00	24.50	23.00	23.00	23.00	23.00	24.00	39.50	55.00	60.00	62.00	62.00
Cl_2 (Total), Cc.	(*w*)	....	....	....	....	....	....	....	7.5	8.5	2.5	0.0	0.0
Cl_2 (Fixed), Cc.	(*x*)	....	....	....	....	....	....	....	0.5	8.5	2.5	0.0	0.0
Cl_2 (Fixed), G. per liter	(*y*)	....	....	....	....	....	....	....	0.00177	0.006035	0.00178	0.00000	0.00000
Cl_2 (Fixed), Per cent	(*z*)	....	....	....	....	....	....	....	6.67	100	100	0.00	0.00

[1] Weight at beginning 57.765 g.; after 120 hrs., 56,9655 g.; loss, 1.4 per cent. [2] All volumes in this table are on the basis of 0.01 *N*.

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[1] Page 655.

[2] *Compt. rend.*, **168** (1919), 1114.

before air was passed through. These points will be considered in detail in the interpretation of the experimental results, where it is shown that it is impossible to establish any correct relationship between Cl_2 and HOCl, and that such work as de Mallman's is distinctly in error unless properly interpreted.

APPROVED METHOD—The method finally adopted as by far the most accurate depends essentially upon the determination of HOCl by means of arsenious acid, and a combination of this result with Methods 1 and 3, together with the usual method for chlorine and hypochlorous acid in the presence of each other, from which the concentration of all three products may be calculated. The arsenious acid method, depending upon oxidation to arsenic acid by hypochlorous acid, is briefly described in such texts as Treadwell, but no work has been done on the effect upon its accuracy of the simultaneous presence of Cl_2 and HOCl. The actual titration is remarkably simple, definite and rapid, and the results have been found to be capable of repeated reproduction from the same solution, since there is no possibility of secondary reactions with indicators. In order to test out the accuracy of this method for determining HOCl alone and in the presence of the other equilibrium products in the solution, the following experiments were performed.

A solution was carefully shaken for several minutes with freshly precipitated mercuric oxide. The oxide was dissolved by the HCl, but the HOCl, being too weak to react, was left free in the solution, which was then titrated with arsenious acid. In a second test, some of the solution was shaken up with pure calcium carbonate, which reacted only with the hydrochloric acid. This solution was then titrated. It is a singular fact that in both of these cases the results checked exactly with those of a straight titration for HOCl in the presence of both Cl_2 and HCl. The titration must, of course, be carried on very rapidly in order to obtain best results.

EFFECT OF TIME—In following the changes in concentration of Cl_2, HOCl, and HCl with time, in the absence and presence of iron, the following process was adopted. The solution was very carefully made up in order to assure uniform composition and kept in tightly stoppered bottles in the thermostat at 25°. Three portions of 50 cc. each were removed at the same time; one was titrated for HOCl by means of 0.01 *N* arsenious acid solution; the second was acidified with 25 cc. 0.01 *N* HCl, NaI added, and the iodine liberated by both Cl_2 and HOCl was titrated with $Na_2S_2O_3$, after which the excess acid was titrated with 0.01 *N* NaOH, using phenolphthalein as indicators; the third was placed in a Drechsel wash bottle, connected with another similar bottle containing NaI solution, and air bubbled through the original solution for 5 or 10 min. in such a way that the evolved gases would pass through the NaI solution. Both were then titrated with sodium thiosulfate.

In Table I are given the results of the best single series of determinations. Part A shows the results with the solution alone, and Part B in the presence of low-carbon steel. The solutions in both cases were exactly the same, and the three series of titrations on both solutions were made at the same time, once every 24 hrs., using standard solutions which had been repeatedly checked in order to assure accuracy. A great many relationships of rather remarkable nature are at once apparent from an examination of this table, of which only the more important will be specifically pointed out. Part A will first be considered.

As an indication of the accuracy and soundness of the method involved and a justification of the interpretation of results, it is noted that the results in several lines check perfectly; *e. g.*, Line *j* giving the back titration with NaOH corresponds with Line *v* which is the same titration on a different solution after the air-bubbling process to remove chlorine. Lines *g* and *u* for chlorine also agree. Another outstanding relationship is that final equilibrium is reached after 48 hrs., and the amounts of *chlorine, hypochlorous acid,* and *hydrochloric acid remain constant* for the duration of the experiment, 120 hrs. There is no reason to doubt the fact that this equilibrium would remain indefinitely in the dark bottle, if conditions were kept constant. This point of equilibrium represents a concentration of 0.008 mole HOCl per liter, 0.00012 equivalents or 0.00006 mole of chlorine per liter; and 0.0035 mole HCl per liter. This gives an equilibrium constant of 0.467 at 25°, considering the concentration of H_2O as constant and the acids completely ionized, which is checked surprisingly well, starting from entirely different concentrations (see Table II). It is a matter of considerable surprise that so relatively great a concentration of HOCl is found, but it is verified by such experiments as titrating before and after exposure of the equilibrium solution to strong sunlight for some time, during which the HOCl is converted to HCl.

TABLE II

				Aëration		
Time Elapsed Hrs.	0.01 *N* As_2O_3 Cc.	0.01 *N* $Na_2S_2O_3$ Cc.	0.01 *N* NaOH Cc.	0.01 *N* $Na_2S_2O_3$ (1) Cc.	0.01 *N* $Na_2S_2O_3$ (2) Cc.	0.01 *N* NaOH Cc.
			A—SOLUTION WITHOUT STEEL			
			Clear Bottle			
0.0	42.70	50.00	23.50	41.00	6.40	18.00
24.0	42.60	46.00	17.00	39.20	7.80	18.00
48.0	38.40	41.00	18.00	33.50	7.50	19.00
72.0	36.50	39.00	19.50	34.00	4.00	19.50
96.0	34.50	35.50	20.00	31.00	4.50	21.00
120.0	31.00	30.50	20.00	26.50	3.50	20.50
			Dark Bottle			
0.0	46.60	54.00	20.50	40.50	14.00	17.80
24.0	49.00	50.50	16.00	41.50	8.50	17.70
48.0	46.00	47.50	18.00	37.50	10.50	17.70
72.0	43.00	45.50	18.50	38.00	6.40	19.00
96.0	42.00	44.00	19.00	37.00	6.50	17.50
120.0	34.00	42.50	18.50	37.00	4.00	17.50
			B—IN PRESENCE OF STEEL			
			Clear Bottle			
0.0	30.50	34.50	10.00	35.00	4.00	10.00
24.0	18.00	26.00	18.00	21.00	2.00	18.50
48.0	5.00	14.00	25.50	10.00	1.50	26.50
72.0	0.00	2.50	35.00	2.50	0.00	35.50
96.0	0.00	0.00	35.20	0.00	0.00	35.50
120.0	0.00	0.00	35.20	0.00	0.00	35.50
			Dark Bottle			
0.0	30.50	33.50	10.00	31.00	2.50	9.00
24.0	20.00	24.00	15.50	20.50	3.50	15.50
48.0	7.50	12.50	24.00	10.00	2.00	23.50
72.0	0.00	2.50	35.00	2.50	0.00	31.80
96.0	0.00	0.00	35.00	0.00	0.00	32.00
120.0	0.00	0.00	35.00	0.00	0.00	32.00

Another observation which may be made on Part A of Table I is the formation of chlorine by decomposition of HOCl with air. After 48 hrs. this total amount of HCl remains constant (Lines *j* and *v*) and also the concentrations of HOCl and Cl_2 (Lines *d* and *i*, and *e* and *r*), but the amount of chlorine which it is possible to remove by bubbling air through the equilibrium solution becomes gradually less. By comparing Lines *b*, *p*, *q*, *s*, and *t*, it is at once apparent that HOCl, at first decomposing to form chlorine to the extent of 16.5 per cent, gradually becomes more stable towards the action of air as time passes, until after 120 hrs. only 3.75 per cent is decomposed to form chlorine. Just what is the explanation of this anomaly is difficult to say. It may be caused by hydration or polymerization, but most likely is connected intimately with the formation and existence of "fixed" chlorine, which will be presently discussed. This same result has been observed with original solutions of all concentrations, but the more dilute the solution, the more stable it is. It is thus possible to prepare a solution of such concentration that it will be impossible to remove any chlorine by the bubbling of air, either as the free gas or by decomposition of HOCl. Solutions which require a maximum of 22 cc. 0.01 *N* $Na_2S_2O_3$ per 50 cc. in determining both hypochlorous acid and chlorine will not give even from the beginning the slightest trace of chlorine in the second bottle. If the solution is strong enough to require 24 cc., it is possible to remove enough chlorine at once to require a fraction of a cc. of $Na_2S_2O_3$ for titration, but in 24 hrs., though the titer of the original solution is still the same, no chlorine is driven over the series of experiments shown in the table the concentration is over twice the minimum for appearance of chlorine, and it is easy to see why there should be some decomposition of hypochlorous acid. As chlorine is removed, of course the equilibrium is displaced in such a way that HOCl and HCl react to form more chlorine. But *HCl remains constant*, which would, therefore, point to the fact that the greatest factor seems to be the *increasing concentration* of "fixed" chlorine, which cannot be removed from solution by aëration. In reality, therefore, the decomposition of HOCl is apparent only and indeterminate. This is even more clearly shown when iron is present and *all* the HOCl disappears.

Part B of Table I shows the extremely interesting effect of iron upon the equilibrium just discussed. Some time after 24 hrs. all the hypochlorous acid disappears, and after 72 hrs. the chlorine disappears, forming hydrochloric acid, which thereafter remains constant in concentration, showing that finally only one equilibrium is involved:

$$FeCl_3 + 3H_2O \rightleftarrows Fe(OH)_3 + 3HCl$$

Lines *j* and *v* again show remarkable agreement. It is to be observed that the ratio of concentrations of HOCl to Cl_2 is at such a value after 24 hrs. that aëration apparently causes complete separation; for Lines *b* and *o*, and *g* and *r* show this. At the next reading, however, HOCl has disappeared, giving no apparent trace with arsenious acid, but 8.5 cc. 0.01 *N* $Na_2S_2O_3$ are still required for the original solution, which can be only chlorine. However, no length of aëration will serve to remove any of this chlorine from solution. This entirely disappears in another 48 hrs., with attendant increase in hydrochloric acid. The Arrhenius theory of active and passive molecules in equilibrium with each other might be very well applied here, but the uncertain catalytic effect of H^+ ions, the formation of hydrogen during reaction with iron, and various possible effects of increasing concentrations of ferrous and ferric salts introduce too many complications. Another plausible explanation of fixed chlorine would be hydrated molecules. The pressure of chlorine gas above a solution is proportional to both the concentration of unhydrated and hydrated molecules, but the proportionality factor is quite different. There is undeniable evidence of the existence of hydrated chlorine in solution. Now, at equilibrium, simply expressed:

$$Cl_2 + H_2O \rightleftarrows Cl_2.H_2O$$

$$\frac{C_{Cl_2} \times C_{H_2O}}{C_{Cl_2.H_2O}} = K$$

But C_{H_2O} may be considered constant, and hence:

$$\frac{C_{Cl_2}}{C_{Cl_2.H_2O}} = K_1 \text{ or } C_{Cl_2} = K_1C_{Cl_2.H_2O}$$

The distribution ratio of unhydrated molecules gives by Henry's law

$$P = K'C_{Cl_2}$$

(where P is pressure of gaseous chlorine).

Combining with the above:

$$P = K'K_1C_{Cl_2.H_2O} = K_2C_{Cl_2.H_2O}$$

Hence K′ and K_2 may be greatly different. Furthermore, the equilibrium is constantly being disturbed because of the existence of another:

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl$$

Under certain conditions of concentration, therefore, a final total effect may be represented by:

$$Cl_2.H_2O \rightleftarrows HCl + HOCl$$

The gaseous pressure would therefore be regulated to the hydrated molecules, and the fugacity of unhydrated molecules would be negligible. This is merely another way of saying, as de Mallman[1] does, that chlorine is fixed in a quantity proportional to the ratio $Cl_2 : H_2O$, and decreasing with increased ratio and also with increasing acid concentration. If we therefore consider as "free" chlorine only that which *can be* removed by aëration—a sort of excess above the proportionality to the ratio $Cl_2 : H_2O$—de Mallman's generalities agree with these experimental results. The impossibility of removing chlorine gas completely from solution in a short time is verified by the work of Olson,[1] just published, on the equilibrium in chlorine-treated water at 91°. This author says that it may be removed "in a few hours," as contrasted with the 5-min. periods of de Mallman. Olson, however, does not take into consideration any possible influences which might cause the chlorine to disappear in a few hours, such as formation of the acids, without being removed by aëration.

THE CORROSION OF LOW-CARBON STEEL BY CHLORINE-TREATED WATER

Table III discloses several interesting relationships. Low-carbon steel bars of similar composition were

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[1] *Loc. cit.*

TABLE III

Kind of Water and Amount of Chlorine	No.	Diameter In.	Length In.	Surface Sq. In.	Weight before Being Acted on Grams	Weight after Being Acted on Grams	Loss in Weight Grams	Loss in Weight Per cent	Bottle Kept in	Weight Lost per Sq. In.
River + 0 Cl_2	1	0.501	3.031	4.77	76.3380	75.9700	0.3680	0.48	Light	0.0771
River + 2 p. p. m. Cl_2	2	0.501	3.14	4.94	76.6648	76.2920	0.3728	0.47	Dark	0.0754
	3	0.501	3.14	4.94	78.5250	78.1100	0.4150	0.53	Light	0.0840
River + 5 p. p. m. Cl_2	4	0.501	3.14	4.94	78.5926	78.2050	0.3876	0.49	Dark	0.0784
	5	0.501	3.14	4.94	78.7923	78.4000	0.3923	0.50	Light	0.0794
River + 10 p. p. m. Cl_2	6	0.501	3.125	4.91	78.3265	77.9700	0.3565	0.45	Dark	0.0726
	7	0.501	3.14	4.94	78.0265	77.6500	0.3765	0.48	Light	0.0762
Reservoir + 0 Cl_2	8	0.501	3.14	4.94	78.5790	78.2500	0.3290	0.42	Light	0.0666
Reservoir + 2 p. p. m. Cl_2	9	0.339	3.094	3.29	36.7735	36.5230	0.2505	0.68	Dark	0.0764
	10	0.339	3.156	3.36	37.5197	37.2300	0.2897	0.77	Light	0.0862
Reservoir + 5 p. p. m. Cl_2	11	0.339	3.156	3.36	37.4256	37.1500	0.2756	0.74	Dark	0.0820
	12	0.339	3.125	3.33	36.9975	36.6960	0.3015	0.82	Light	0.0905
Reservoir + 10 p. p. m. Cl_2	13	0.339	3.047	3.25	36.4015	36.1260	0.2755	0.76	Dark	0.0878
	14	0.339	3.156	3.36	37.2968	37.0060	0.2908	0.78	Light	0.0865
Distilled + 0 Cl_2	15	0.339	3.125	3.33	37.0810	36.7500	0.3310	0.89	Light	0.0994
Distilled + 2 p. p. m. Cl_2	16	0.339	3.125	3.33	37.1517	36.8100	0.3417	0.92	Dark	0.1026
	17	0.339	3.125	3.33	37.3310	36.9910	0.3400	0.91	Light	0.1021
Distilled + 5 p. p. m. Cl_2	18	0.339	3.156	3.36	38.0679	37.7430	0.3249	0.86	Dark	0.0966
	19	0.339	3.125	3.33	37.2250	36.8830	0.3420	0.92	Light	0.1026
Distilled + 10 p. p. m. Cl_2	20	0.339	3.125	3.33	37.2095	36.9300	0.2795	0.75	Dark	0.0839
	21	0.339	3.156	3.36	37.5665	37.1720	0.3945	1.06	Light	0.1174

placed in solutions of different kinds, and kept in sealed bottles in the light or dark for 100 days. The adhering rust was then carefully removed without abrasion of the unaffected metal, dried at 102°, and reweighed. The loss in weight could then be determined; though more pertinent for purposes of comparison are the results in the weight lost per square inch of original surface. It is at once apparent that greater loss has been sustained in the light than in the dark, due of course to the greater completeness of reactions involving the decomposition of HOCl in light, to form HCl and oxygen. It is also evident that, considering each type of solution separately, rusting or oxidation usually increased with increase in chlorine content, and that corrosion increased in the order: river, reservoir,[1] distilled water.

The least rusting effect is shown by reservoir water containing no chlorine, in the following ratio: reservoir 0.0666, river 0.0771, distilled 0.0994. For the solutions containing chlorine, the least active is river water with 10 p. p. m. chlorine in the dark, and the most active is distilled water with the *same concentration* of chlorine in light. This wide difference is a clear indication of the profound effect of dissolved electrolytes upon the chlorine equilibrium and upon the iron oxidations. Solutions having apparently the same effects are:

2 parts in river water, light, and 10 parts in distilled, dark
0 part in river water, light, and 10 parts in river, light
10 parts in river water, light, and 2 parts in reservoir, dark
2 parts in reservoir water, light, and 10 parts in reservoir, light
2 parts in distilled water, both light and dark, and 5 parts in distilled, light

Because of the extremely great influence of variations of the structure of the steel, rigorous conclusions are not, of course, justified, aside from the general points already considered. After the rust coating was removed at the end of the experiment, the steel bars presented a peculiar spotted appearance, varying from one specimen to another in the ratio of dark area to bright. The corrosion clearly took place on the bright areas, while the dark areas presented very largely the appearance of the original bar with a very tenacious layer of oxide. This differential corrosion in a solution of uniform constitution in which there was uniform contact can be accounted for only by the heat treatment of the original steel, which was probably cold-rolled, so that electrolysis resulted. There was no evidence of any marked pitting due to segregation in the steel structure; hence the effect must be due to heat treatment.

This very delicate test of the uniformity of steel was even more markedly shown by the following experiment. Two highly polished steel bars from the same piece and of the same size were suspended by means of platinum wire in a solution of chlorine in water. One of the bars had been previously rendered passive by immersing in fuming nitric acid, while the other was left active. After 5 min. small bubbles of gas were apparent on the surface of the active bar, and in 15 min. there appeared quite sharply the peculiar mottled condition just described, in which the bright and dark areas were extremely well defined, though the differentiation gradually faded somewhat. The passive bar presented no such phenomenon, though corrosion ultimately set in to much the same extent as with the active bar.

The general average effect of the city water of Nashville upon low-carbon steel containers, such as pipe, is to be found between Nos. 9 and 10 in Table III (reservoir water containing on the average 2 p. p. m. of chlorine), or a corrosive effect of perhaps something over 0.7 per cent loss in 100 days. This supposes that there is to be found no great segregation, which would result in much greater local corrosions, and that outside electrolytes in ground water are not in the action. As a matter of fact, however, the presence of strong local circuits about underground pipes will result in a much greater and much less uniform corrosion than is to be observed in this study made under the most ideal conditions. Flow of water tending to remove adhering rust and presenting new surfaces will also have a large effect. However, in this case of water flowing through a pipe continuously, the electrical conditions are very much more uniform than outside the pipe, and rusting from the inside is always negligible compared with that on the outside, where there may be intermittent exposure to water.

It has been further confirmed that iron subjected to

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[1] Reservoir water is simply the river water treated with alum in settling tanks.

strain or uneven treatment corrodes much more readily than that which has been treated uniformly, the strained part being electropositive to the unstrained. In addition to the differential corrosion due to cold rolling of the bars, there was indication of small grooves parallel to the long axis, due to drawing and resultant minute differences in mechanical strain. Now, in order that rust may be formed, the metal must first go into solution and hydrogen be given off in the presence of oxygen or certain oxidizing agents, thus presuming electrolytic action, as every metallic ion that appears at a certain spot demands the disappearance of a hydrogen ion at another. Iron possesses a specific electrolytic solution tension with regard to a solution of chlorine in water, so that solution results until the osmotic pressure counterbalances the solution pressure. This latter is influenced by segregation, crystal form as related to heat treatment, impurities, temperature, and, of course, the strength of the chlorine solution, and the relative quantities of Cl_2, HOCl, HCl, and, under some conditions as previously shown, hydrated chlorine. It scarcely requires mention that in steel different portions of the same bar, even a very few centimeters apart, possess different solution tensions and behave like different metals if immersed in an ionized solution. In the consequent electrolysis, the ferrous ions liberated at the anodes undergo secondary chemical changes in the presence of such activating agents as chlorides or dissolved oxygen or chlorine itself—the latter two of which act in the very important role of depolarizers—resulting in hydrated ferric oxides, which are formed with a speed of reaction infinitely great in comparison with the other processes.

SUMMARY

Rusting occurs in distilled water without chlorine because of the presence of dissolved oxygen, which is of course present in greater quantity than in water containing dissolved electrolytes. In the presence of chlorine, the most active agent is of course HOCl, which, it has been shown, disappears first from the solution. There is no question but that the rust is formed rapidly during the disappearance of HOCl, and then practically stops when the concentration of HCl becomes constant, as shown in Table I. This indicates an equilibrium:

$$FeCl_3 + 3H_2O \rightleftarrows Fe(OH)_3 + 3HCl$$

The presence of $FeCl_3$ in solution is of course easily verified.

It has been shown that the reaction

$$H_2O + Cl_2 \rightleftarrows HOCl + HCl$$

proceeds only very slowly and comes to equilibrium, the constant of which has been roughly determined. It has further been shown that iron has an apparent catalytic action on the reaction, resulting in the disappearance of both chlorine and hypochlorous acid. This has been verified by the very recent work of Olson[1] on the same reaction, carried out at 91° so that $HClO_3$ would be formed. It is pointed out in that work that in order to act as a catalyst the iron must of course exist in two stages of oxidation, and Fe^{++} must reduce ClO^- ion faster than $Cl^=$ does, together with the necessity for a fast enough reduction of Fe^{+++} by Cl^- ion in order to maintain an effective concentration of Fe^{++}. In deciding whether or not the iron has actually acted as a catalyst in materially hastening the final attainment of the equilibrium

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl,$$

it is at once apparent that, in the presence of chloride, the iron is *almost completely* in the form of the ferric ion, and hence the effective concentration of ferrous ion which can react with ClO^- is negligibly small. The effect is, therefore, practically entirely chemical rather than catalytic in nature, since the equilibrium is entirely destroyed and two of the members disappear.

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[1] *J. Am. Chem. Soc.*, **42** (1920), 896.

ADDRESSES AND CONTRIBUTED ARTICLES

CHEMISTRY'S CONTRIBUTION TO THE LIFE SCIENCES[1]

By A. S. Loevenhart

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THE SERVICE TO BIOLOGY AND MEDICINE OF STUDIES ON OXIDATION

All biological science rests on a tripod of physics, chemistry, and a residual leg of biology which includes all the factors which cannot at present be reduced to the more exact sciences. So intimate is the relation of chemistry to biology and medicine that it is inconceivable that any great advance could be made in chemistry without being reflected in the superimposed structures. I should like to point out the effect on these subjects of two great advances in chemistry. Modern chemistry may be said to have begun with the overthrow of the phlogiston theory of combustion by Lavoisier and the establishment of the mechanism of combustion and oxidation. With this, chemical physiology became a possibility. Oxidation is the only energy-yielding process known to occur to any extent in the body. The hydrolyses and hydrosyntheses which occur in the body are practically isothermic reactions. Lavoisier was not a physiologist, but the relation between oxidation and respiration is so very close that Lavoisier associated with himself the physiologist Sequin, and in their joint article they stated that the bronchi exude a hydrocarbonous fluid and that this is burned in the lungs. They believed that vital oxidation is exactly similar to combustion, that oxidizable material in the body is brought to the lungs and there burned in contact with the oxygen inhaled, the lungs acting as a sort of furnace. Spallanzani first showed that all tissues absorb oxygen and produce carbon dioxide, and through the work of many men it was established that oxygen is absorbed by the blood in passing through the lungs and carried to the tissues where oxidation really occurs. In the effort to determine why such stable substances as proteins, carbohydrates, and fats are burned in the body at a temperature of 37° the group of catalytic agents known as the oxidizing enzymes or oxidases was discovered. The work on the digestive enzymes and the oxidases proved to be the greatest stimulus to the study of the whole subject of catalysis, which has become so immensely important in every phase of chemistry. It is obvious that it was necessary to understand the nature of

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[1] Presented at the General Session of the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

combustion before vital oxidation could be attacked. The recent work on slow oxidation and the peroxide theory of oxidation of Traube, Baeyer, Engler, and many others emphasize the differences between vital oxidation and combustion.

A. S. LOEVENHART

There are many phases to the subject of vital oxidation, which may be divided as follows:

(1) The mechanism by which oxidation is brought about in living matter, including the subject of the oxidizing enzymes.

(2) The nature of substances capable of being oxidized by living matter. Thus it is known that certain substances which are readily oxidized outside the body, such as carbon monoxide and oxalic acid, escape oxidation in the living organisms.

(3) The relation of chemical constitution to oxidizability in the body. Thus it is known that, whereas *d*-glucose and *d*-fructose are readily oxidized in the body, *l*-glucose and *l*-fructose escape oxidation entirely. Apart from the stereochemical relation, constitution is often the determining factor in oxidizability.

(4) The relation of oxidation to the energy requirements of the organism.

(5) The relation of oxidation to other chemical processes occurring in the organism. Thus when oxidation is interfered with, abnormal products of metabolism may result.

(6) The effect of various substances and conditions on vital oxidation.

(7) The relation of oxidation to vital activity, by which is meant the relation of oxidation to stimulation and depression, including the symptoms and morphological changes produced in the tissues as a result of alteration in oxidation.

(8) The question whether any substance other than molecular oxygen can furnish the body with physiologically available oxygen.

ORGANIC PEROXIDES IN MEDICINE

It is obviously impossible to discuss these various phases of oxidation in the time at our disposal, and I desire only to indicate the great scope and interest connected with this subject. I should, however, like to say that the analogy of the organic peroxides and of the oxidases, first pointed out by Kastle and Loevenhart,[1] is interesting from a chemical point of view. Furthermore, the group of organic peroxides and other organic oxidizing agents are interesting and important from another standpoint. During the war the most important and useful antiseptic substances proved to be those whose antiseptic activity is attributable to their oxidizing properties—the hypochlorites and the chloramines. The antiseptic action of these substances is not interfered with by the presence of protein, to which is attributable their great merit as antiseptics for wounds. Furthermore, it has been shown by Hektoen[1] that certain oxidizing substances greatly increase the formation of certain bodies of an antitoxin-like character. This would lead us to believe that oxidation plays an important role in the process of immunity to disease. Amberg[2] has shown that certain organic oxidizing substances markedly reduce the local inflammatory reaction to such irritants as mustard oil, and Arkin[3] has likewise shown that they stimulate phagocytosis.

It may be that we shall here find an antiseptic which can be administered intravenously in bacterial blood infections. It is probable that these substances will prove valuable not so much in consequence of their antiseptic action, but rather by the stimulation of natural immunological processes, that is, the production of antitoxins, and bacteriolysins, and the stimulation of phagocytosis. You are, of course, aware that we have no drug at the present time which is useful in general bacterial infections. In all those cases in which we have specific substances which are useful in general infections, such as syphilis, relapsing fever, and malaria, the infectious agent is a protozoan and not a bacterium. Such a substance would be a boon to mankind.

Both from the standpoint of the development of important antiseptics and substances useful in the treatment of infection, and also from the standpoint of the elucidation of biological oxidation, I believe the organic peroxides to be a most important group requiring further work on the part of the pure chemist. We should know more of the possible methods of preparing these substances, and a much larger number should be prepared than are at present known. We need to investigate many such substances in order to arrive at one having exactly the right properties. Thus if the substance be too active an oxidizing agent, it will be toxic and, on intravenous injection, it may alter the blood pigment, or it may be used up in oxidizing substances in the blood so that it will not reach the tissues. Furthermore, the substance should be soluble in water, and, as a wound antiseptic, it would be a great advantage if it were soluble in glycerol. I am inclined to believe that those substances whose oxidizing action is due to the presence of oxygen would prove to be more valuable than those substances whose oxidizing action is due to the presence of chlorine.

Let us pass on to another chemical achievement and observe its effect upon pharmacology and medicine. The treatment of disease by drugs reaches back into remotest antiquity. The earliest documents extant tell of the uses of drugs and poisons. Various views have been expressed regarding the origin of the belief in the efficacy of drugs in the treatment of disease. From the vile and revolting character of many remedies which have been used, it has been suggested that it had its origin in the belief that diseases are sent by a Deity, and that revolting things were used as a sacrifice to appease the wrath of the Deity. Against this view is the oft-repeated observation that carnivorous animals at times instinctively consume certain plants. Then again, many remedies are used by primitive peoples which are in no sense offensive. It may be that the view held sway that since the Lord created all things, including diseases, and sent them to punish man, He must have placed in the world a cure for all diseases and left it to the ingenuity of man to find the remedy. At any rate, when illness plagues a man, he and his family are so constituted that they will search for a remedy as long as life lasts, and in the course of human history it is hardly possible to find an accessible substance which has not been used in the treatment of almost every disease. They proved all things but it was impossible to hold fast only to that which was good. Their observations were crude and faulty. Every case was treated and no one knew what the course of the untreated disease would be, and yet by this method great ad-

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[1] *Am. Chem. J.*, **26** (1901), 539; *Therap. Monatsh.*, **19** (1905), 426.

[1] *Trans. Chicago Pathol. Soc.*, **8** (1911).

[2] *Z. Exp. Med.*, **2** (1913), 19; *J. Pharmacol.*, **10** (1917), 209.

[3] *J Infect. Dis.*, **11** (1912), 427.

vances were made in the course of the ages. Thus, opium was introduced into medicine before the Christian era, and cinchona bark in the treatment of malaria, and mercury in the treatment of syphilis were introduced by the same method at a much later period, but their introduction antedated scientific medicine or chemistry.

THE DEVELOPMENT OF CHEMOTHERAPY

The second great chemical achievement whose effect on pharmacology and medicine I desire to discuss briefly was the isolation of the alkaloids of the plants in the first half of the last century. With this achievement, medicine took a great step forward and it is difficult to realize its service in the field of medicine. This work made it possible to assay some of the important crude drugs chemically, the pure principles could be employed when indicated, dosage became more accurate, and it prepared the way to hypodermic medication. Following the isolation of the alkaloids, their composition was determined and, with the rise of organic chemistry, the problem of their constitution presented itself. Although all these substances are complicated, great advances have been made in the study of their constitution, and in some instances it has been completely solved. When the chemist had determined the constitution of these substances, pharmacologists began to inquire into the cause of their remarkable biological properties and sought to determine the groups within the molecule responsible for them. This led to the production of other closely related substances, and some of these artificial substances have proved to be more useful than those occurring in nature. This work naturally developed into the general proposition of determining the relation of chemical constitution to pharmacological action. This subject came into greatest prominence with the investigations of Ehrlich and his co-workers, who introduced the term chemotherapy to signify this field of work. Ehrlich started out with the proposition that arsenilic acid is useful in the treatment of spirillar infections, including the diseases caused by the trypanosomes and the *treponema palladum*, the latter being the infectious agent in syphilis. Starting out with arsenilic acid, they proceeded to vary the compound in every conceivable way and to determine what particular grouping possessed the greatest therapeutic power against these infections. The 606th substance studied proved to be arsphenamine (salvarsan), the most valuable drug that has been produced in the treatment of syphilis. This substance had the disadvantage of being difficultly soluble in water, so that its administration presented considerable difficulty. In order to determine how the substance might be rendered soluble without destroying its therapeutic value, the work was continued, and after about 350 more substances were prepared they struck upon neoarsphenamine (neosalvarsan). This is by no means, however, the last word in the treatment of syphilis. The beautiful work of Jacobs and Heidelberger on the chemical side, and of Brown and Pearce on the biological side, at the Rockefeller Institute, will surely result in the introduction of certain compounds which will be of great value in the treatment of certain types of syphilis. The interest to us in all this work is, first, that it is of the greatest possible practical importance to humanity and, second, that it requires the most complete coöperation between organic chemists, pharmacologists, and physicians. To my mind, it is today the most promising field in any of these subjects. The difficulty presented is in getting full coöperation between these groups of workers. This difficulty, although great, must be overcome. It will require large appropriations, as appropriations go, for scientific work, and the men engaged in it must be willing to pool their interests and have full confidence in one another. I think we scientific men are too often thought of as being of the prima donna type, each one insisting that he shall be the whole show. I am sure that this is a calumny and that in the search of valuable new drugs, groups can easily be formed of men who will be willing to pool their interests and each one receive simply his share of credit for the success in the work. Those of us who were engaged in the research work of the Chemical Warfare Service must certainly have been impressed with the effective work done by the chemists and pharmacologists working in close coöperation. It is a remarkable fact that we actually know more about the pharmacological effects of certain groups of substances, which were worked on only for a brief period of one year and which were designed for the destruction of human life, than we know about the most important substances which have been used in the treatment of human disease for a period of 2000 years. Men working in time of war with the exaltation of patriotism were willing to coöperate; the exaltation of relieving human suffering should certainly be no less, and we must look forward to the formation of many groups of workers in this field if we are to fulfil our obligation to society.

CHEMICAL TRAINING FOR THE MEDICAL RESEARCH WORKER

Perhaps I may be permitted to say a word in conclusion regarding the importance of chemical training for those who are going into medicine, and especially those who are going into the research side of medicine and the medical sciences. Every research man in medicine should receive a most thorough training in one of the fundamental sciences upon which his work rests. It may be either chemistry or physics; it cannot be both, because each of these subjects is too great for a man really to become expert in both. It has been my experience that a man cannot become a real chemist, develop the best chemical technique, and, above all, the chemical point of view and mode of thought, after going into biology. It would seem that a chemical training cannot often be superimposed upon biological training, but must precede it just as the foundation must precede the construction of a building. The reason for this is not clear to me, but it may be that the biological work when once entered upon seriously is so enthralling that it is impossible for one to go back and so deeply immerse himself in chemistry as to absorb its spirit. A man can hardly develop into a high type of chemist simply as a means to an end; for the time being it must be studied for its own sake. It amounts virtually to this, that more chemists must go into medicine and the medical sciences. The man must first become a chemist or a physicist, and later a physician. With the mere rudiments of chemistry which the average medical student receives we must be satisfied for the present, because the medical curriculum is very full, but for those who are going to advance medicine from the experimental side in the future, we should advise that they be professional chemists or physicists first.

THE SUGAR INDUSTRY OF FRANCE SINCE THE WAR[1]

By T. H. Murphy[2]

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As Chief of the Sugar Division, Engineering Section, of the War Damage Board, American Commission to Negotiate Peace, the author was assigned the task of estimating the damage done by the war to the sugar industry of France. M. Saillard, chief chemist of the Association of Sugar Manufacturers of France, was consulted in his splendid laboratory. M. Veuville, the president of the association, furnished a letter of introduction which proved very useful. M. Barbarre, designer and builder of sugar factories, M. Gilbert, manager of the largest beet-sugar factory in France, and M. Alexander, editor of the *Journal of the Sugar Manufacturers*, gave helpful advice and furnished invaluable data and statistics.

The continental blockade, in 1806, prevented the entry of colonial cane sugars into Europe, and the occasion was seized

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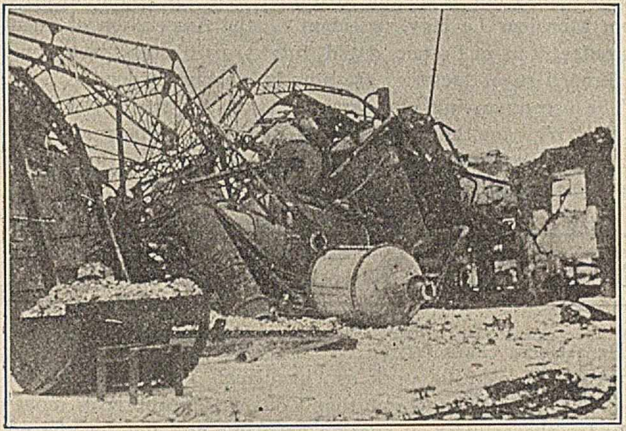
[1] Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] Formerly Major, Chemical Warfare Service, A. E. F.

by Delessert and Mathieu de Dombasle to perfect the experiments of Achard, and the first French sugar factory was installed. Napoleon recognized the value to the nation of the new industry and granted subsidies and complete exemption from taxation. Later, the blockade was raised and Europe was flooded with cane sugar, and it was not until the Restoration and the Second Empire that the beet-sugar industry triumphed; but from that time on it made rapid and certain progress.



Sugar Factory of Montescourt-Lizerolles—Department Aisne, Arrondissement de St. Quentin

The extent to which the French sugar industry had grown before the war is shown by the fact that 7 per cent of the capital invested in industry in the invaded regions of Northern France was placed in the sugar industry. The extent of the damage suffered is shown by the fact that, out of 217 sugar factories in France in 1913, over 142 were damaged, and, for the most part, completely destroyed. Measured on the basis of production in tons, 66 per cent of the sugar industry of France was wiped out.

There were in operation in 1913, 213 sugar factories; and in 1917, only 65. In 1913 there were produced 877,656 metric tons of refined sugar, and in 1917 only 185,000 tons. In 1913 the balance of the sugar trade showed 78,739 tons of surplus sugar exported; and in 1917, 397,746 tons imported, with a decrease in consumption from 703,126 tons to 563,479 tons. The sugar shortage of France is about 716,132 tons per year since the loss of her factories.

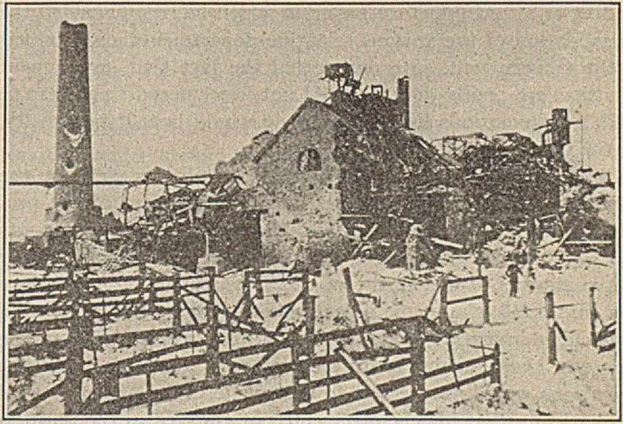
The 142 sugar factories which were in the war area were damaged, on the average, to the extent of being 85 per cent destroyed; and to rebuild them or replace them at present prices of machinery and building materials, would cost about $89,000,000. The land remains and building materials exist, but the grounds and buildings represent only about one-half of the value of the average beet-sugar factory. The machinery and mechanical appliances represent the other half, or a value of $45,000,000, but their replacement from other parts of France is impossible for the present. The great steel mills, foundries, engine works, and factories where sugar machinery and equipment were made, were, for the most part, located in the same region, notably around St. Quentin, Lille, and Douai, and these great industrial plants suffered the same fate as the sugar factories.

It is hoped that it will not be out of place to repeat here a portion of a report written by the author while still in France, which was quoted by Major Charles P. Wood, in the March issue of *Sugar*.

> During the 1914 advance of the German armies, very little damage was done to the sugar industry, but, on the other hand, due to the scarcity of metals and materials in Germany in 1917 and 1918, every factory which was behind the 1918 line of maximum advance was absolutely stripped of all copper, brass, bronze, belting, rubber, and electrical equipment. The copper coils, brass plates, and bronze tubes of pans, evaporator effects, juice heaters, etc., were removed; sometimes by unbolting the bottom of the pan or effect, and letting it fall to the floor below, and then removing tubes, coils, etc., through the bottom; and often by tearing away the insulation, and cutting a large section out of the side of the pan or effect by means of an oxy-acetylene flame, and removing the copper and bronze from the interior through this hole. The sugar boiler's brass proof sticks, the brass stuffing boxes, the brass frames of peep glasses of pans, evaporator effects, etc., the copper-lined spouts and troughs of juice filter presses, all centrifugal screens and back screens, all brass and bronze bearings on engines, pulley shafts, etc., were removed by unbolting or breaking off. All electric generators, alternators, motors, distribution boards, etc., were removed, a loss which, in various cases, amounted to 16, 25, 50, and as high as 65 motors for one factory.

The French factories were, in general, good and compared quite favorably with the general run of American factories. Machines were well made, well installed, and conservatively operated. In France, a sugar factory works about 90 to 110 per cent of its rated capacity. The beet-sugar factories of our largest American firm handle, year in and year out, about 170 per cent of their rated capacity. Consequently, it can be seen that to produce a given quantity of sugar requires more machinery and equipment in France than in America. There exists a contrast between French and American methods in the matter of *raperies* or juice annexes. These annexes have boilers, cutters, and a diffusion battery, and pump the diffusion juice through a small pipe line to the central factory. In America very few juice annexes exist, probably only the one in Idaho; but in France they are quite general. The 142 factories destroyed in Northern France had 70 juice annexes which suffered the same fate. One factory, a 3,000-ton mill near Cambrai, had 14 juice annexes situated around the central factory, at distances varying from 1 to 15 miles.

Another contrast exists in the matter of product. While practically all the American sugar factories and refineries, including even the smallest beet-sugar factories in the West, produce white granulated sugar, the general run of French factories produced white crystals, or No. 3 sugar, which was shipped to a refinery. The refineries put out very little granulated sugar, their product being in the form of domino sugar or cubes. The largest refinery in France puts all of its 1,500 tons per day through the "Adant" system, of which the product is 85 per cent domino, and the remaining 15 per cent powder and small broken lumps, incidental to the manufacture of domino. The coast refineries which handle the raw cane sugar from Africa and the French colonies make principally the *pain de sucre* or sugar loaf, a hard conical lump of refined sugar, weighing 2



Sugar Factory of Tricot—Department Oise, Arrondissement de Clermont—between 1914 and 1918 Lines According to Maps, Destroyed in Battles of June 1918 kilograms. This product is demanded principally by the colonial trade.

The French manufacturers and refiners make and sell whatever their trade demands; which, so far, has been principally the sugar loaf and domino; and it is quite likely that when bans are lifted, so that they can buy machinery and equipment outside, they will proceed to reëstablish along the same general lines that existed before the war. Reconstruction presents enormous difficulties, and will doubtless entail long delays, but sooner or later the French factories will be rebuilt.

At the present time reconstruction in France is making enormous strides.

Of the 7,000,000 acres of arable land laid waste by the war already over half has been again put under cultivation. 2163 kilometers of railroad, together with bridges, tunnels and locomotives were completely destroyed, and to-day circulation has been restored over the whole; out of 600 bridges destroyed, 475 have been rebuilt; out of 370 passenger stations destroyed, 200 have been rebuilt; out of 11,500 factories destroyed, 3500 have been rebuilt and 3500 are now under construction. In 1919 France had to import 150,000,000 bushels of wheat, and in 1920 she is having to import only 30,000,000.

This is really wonderful progress in reconstruction, but the sugar industry, because of its requirements in specially constructed machinery and mechanical appliances, because of the enormous amounts of copper, brass, and electrical equipment required, has not been able to do so well. A communication from Monsieur Le Hay, president of the Association of Sugar Manufacturers of France, dated July 5, 1920, states that only 60 French sugar factories are now in working order.

The accompanying photographs, taken by the writer while on field trips for the War Damage Board, in January and February of 1919, will show clearly the average condition of 142 sugar factories after the war.

SCIENTIFIC SOCIETIES

PROPOSED NEW DEPARTURES IN GOVERNMENT CHEMICAL WORK

Dr. F. G. Cottrell, director of the Bureau of Mines, and Dr. C. L. Alsberg, chief of the Bureau of Chemistry of the U. S. Department of Agriculture, faced an audience that was quite generally out of sympathy with the proposed plan to provide government machinery for developing inventions of scientific workers in the various laboratories of the Government, on Friday evening, October 15, 1920, at the Chemists' Club of New York. They had been invited to present their views on this subject before a joint meeting of the American Institute of Chemical Engineers, the American Section of the Society of Chemical Industry, the New York Section of the American Chemical Society, and the New York Section of the American Electrochemical Society. The meeting was largely attended by representatives of the chemical and allied industries, many of whom had come prepared to discuss the subject and express their views in opposition to the proposed plan.

Dr. David Wesson, president of the American Institute of Chemical Engineers, who presided, opened the meeting with the reading of an introductory paper, in which he recommended the consolidation of the various scientific departments and bureaus of the Government. He deprecated the fact that government scientists are poorly paid, but did not favor permitting them to work out inventions from which they would benefit personally, on the Government's time.

Dr. Alsberg was then called upon to present his views on the issue, and he asserted that much misunderstanding of the proposed measure had resulted from incorrect newspaper accounts of what was the true intent of the legislation desired. As far as the Bureau of Chemistry of the Department of Agriculture was concerned, the whole object was to provide some means of developing inventions made by laboratory workers during the course of their regular routine or research work, so that these inventions would not be lost to the public. Dr. Alsberg stated emphatically that his chemists were not engaged in the business of inventing, but, as is the case with every laboratory staff that is efficient, they could not help developing new ideas and processes in the course of their investigational work. In order that such "by-product inventions," which might often prove of great value to industry, should not be lost to the public, it was proposed to create machinery for developing them and incidentally to provide some reward to the inventor. In his Bureau Dr. Alsberg had organized the office of development to take charge of such work, not with the view of competing with any industry, but rather to bring the matter to that stage which would insure for it a proper reception on the part of the industry.

Dr. Alsberg characterized Dr. Wesson's plan of consolidating government scientific work as "inefficient, ineffective and impossible." He pointed out that Congress appropriates money only for the solution of specific problems and not for the advancement of the sum total of human knowledge of the various sciences. Hence all government laboratory work must be of a practical nature and must be performed by experts in each particular field. It would be illogical, for instance, Dr. Alsberg maintained, to have work on mining problems, paper and pulp, fertilizers, and therapeutic serums all referred to a central laboratory and expect expert treatment of it. Coördination is needed, but not fusion, said Dr. Alsberg. He further remarked that it is a mistake to compare the Government to a corporation. It can be compared only to a holding corporation which exercises supervision over the policy of a large group of corporations. Turning again to the subject of developing inventions of government laboratory workers, he stated that his turnover of chemists in the past year had amounted to nearly 40 per cent, due largely to the fact that the salaries paid are not adequate and that no adequate inducement is offered to hold good men in the service. He dwelt on the fact that very often chemists of the Bureau while coöperating with certain industries see glaring examples of waste and inefficiency for which they are able to provide a remedy by marshaling information they have acquired in the course of their experimental work. Some practical method should be found whereby such developments may be passed along for the benefit of all. He cited the discovery of the effectiveness of calcium arsenate in combating the boll weevil as an example of governmental invention, and stated that all methods of preparing this compound had been patented by the Government in order that no one should be obliged to pay tribute to a private concern or individual for using these patents, as had been the case with lead arsenate.

In conclusion Dr. Alsberg stated that the proposed plan of developing inventions of government employees was the result of considerable thought given to the subject by government officials, who were confronted with conditions and not with theories, and who were endeavoring to solve the problem in a manner calculated to redound to the greatest good of their employers, the American public.

Dr. Cottrell was then asked by the chairman to present his views on this important subject, and after discussing the object of granting patents in general and laying emphasis on the fact that patents are granted to promote progress in science and useful arts rather than to reward inventors, he took up the bill before Congress in detail. He stated that the feeling existing in some quarters, that there had been an attempt on the part of those interested in the bill to push it through without giving its provisions proper publicity, was not founded on fact. He related the efforts which had been made to secure publicity for the measure in trade journals and elsewhere without success.

The measure under discussion passed the Senate on March 22, 1920, as Senate bill 3223, and was introduced in the House of Representatives, where it was referred to the Committee on Patents. This committee having before it a bill known as the Nolan bill, which provides for reorganization of the Patent Office, decided to tack the provisions of Senate bill 3223 onto the Nolan bill or H. R. 11984, making it Section 10 of that bill. This bill was passed and then sent to the Senate. During all this time, little or no comment on the matter of promoting government inventions had been aroused, but as soon as the amended Nolan bill with the invention provisions reached the Senate, a number of amendments were suggested, and Congress adjourned before final action was taken on the bill, although the Senate on June 4 passed certain amendments to Section 10. The matter in italics in the following text was eliminated by the Senate amendment while the matter in capitals was added. Therefore, by ignoring italicized portions and reading the capitalized portion as part of the bill the reader has the wording of the bill as it will go to the Conference in December 1920.

SECTION 10. That the Federal Trade Commission be, and hereby is, authorized and empowered to accept assignment of, *or license or other rights or powers under, to develop, to issue or refuse to issue licenses under, to encourage the industrial use and application of, and otherwise to administer,* on behalf of the United States under such regulations and in such manner as the President shall prescribe, inventions, patents and patent rights which said commission deems it to the advantage of the public to be so accepted, as these may from time to time be tendered it by employees of the various departments or other establishments of the Government, *or by other individuals or agencies;* and to coöperate, as necessity may arise, with scientific or otner agencies of the Government in the discharge of the duties herein set out, and the Federal Trade Commission is hereby authorized and empowered to LICENSE AND collect fees and royalties for licensing said inventions, patents and patent rights in such amounts and in such manner as the President shall direct, and shall deposit the same with the Treasurer of the United States; and of the total amount of such fees and royalties so deposited a certain percentum, to be determined by the President, shall be reserved, set aside, and appropriated as a special fund to be disbursed as directed by the President to remunerate inventors for such of their inventions, patents and patent rights contemplated by this section as may prove meritorious and of public benefit; PROVIDED, THAT NOTHING HEREIN SHALL BE CONSTRUED TO GIVE SAID COMMISSION OR ANY OTHER GOVERNMENTAL AGENCY ANY AUTHORITY TO ENGAGE IN THE MANUFACTURE OF ANY SUCH INVENTION OR PATENTED ARTICLE.

The Commissioner of Patents is hereby directed to grant all patents and record all assignments and licenses contemplated by this section without the payment of any fee.

Dr. Cottrell said a great deal of the opposition to the measure that has developed seems to hinge on the fact that the Federal Trade Commission has been designated to handle these inventions. He did not feel that lack of confidence on the part of some in the Federal Trade Commission should be considered sufficient cause to abandon the plan. If the Federal Trade Commission has not fulfilled all that was expected of it, said Dr. Cottrell, steps may be taken to reorganize it, but it is wrong to attempt classifying the work under any other head than this Commission.

He compared the present situation to the condition that has confronted universities and colleges where pure scientific research work carried on in the laboratories often leads to discoveries of commercial value. To develop these the Research Corporation was organized several years ago, and it has been functioning with success. Congress, however, objects to turning over government problems to quasi-public bodies, preferring to tie up all government development work with a regularly constituted governmental agency. It became necessary, therefore, in connection with this legislation, either to create a new organization to handle the patents or to rely on an existing agency such as the Federal Trade Commission which, according to Dr. Cottrell, is the logical agency in this case.

There is nothing mandatory in the bill, declared Dr. Cottrell. Its provisions should be carefully studied, and it is particularly important to establish a fair basis of remuneration for the inventor. Pooling the returns in one fund to be shared equally under specified conditions by the inventors seems to be fairer in Dr. Cottrell's opinion than to reward the inventor with a return based on the financial yield from his specific invention. In conclusion he denied the allegation that the Government intends to compete with private industries and is seeking the passage of the bill before Congress to this end.

The discussion was opened by R. P. Perry who asserted that the passage of the legislation under discussion and carrying out its provisions to their logical conclusion would help the chemical industries of the rest of the world at the expense of those of our own country. He bitterly denounced any attempt on the part of the Government to place itself in competition with private enterprise. He also felt that the proposed legislation would give government employees an unfair advantage over other scientists in the matter of securing patents. In Mr. Perry's opinion the proposed legislation is not desired either by chemists, the industries, or the people. Messrs. H. A. Huston, Sperry, and Weston were strong in their convictions that the Government should keep hands off patent development, and should continue to give service through its various bureaus rather than attempt to establish any form of patent control or license system.

Dr. H. E. Howe suggested that constructive criticism and suggestions be offered by those assembled so that a satisfactory solution to the problem might be arrived at. No further comments of a constructive nature were forthcoming, however. The meeting closed with short statements by both Dr. Cottrell and Dr. Alsberg in which they reiterated their position with regard to the proposed legislation and asked the representatives of industry to study the matter thoroughly and give constructive suggestions for meeting the condition which confronts the directors of our government laboratories in taking care of the inventions of their laboratory workers.

GRASSELLI MEDAL AWARD

At the joint meeting of the American Section of the Society of Chemical Industry with the New York Section of the Société de Chimie Industrielle, held in Rumford Hall, Chemists' Club, New York City, on Friday evening, October 8, 1920, the first Grasselli medal was awarded to Dr. Allen Rogers, for his paper entitled "Industrial Uses for the Shark and Porpoise."[1]

The medal was established in 1919 by the Grasselli Chemical Company of Cleveland, Ohio, to be awarded annually for the paper presented before this Section of the Society of Chemical Industry which should, in the opinion of the Medal Committee, offer the most useful suggestions in applied chemistry. The presentation was made by Dr. Marston Taylor Bogert.

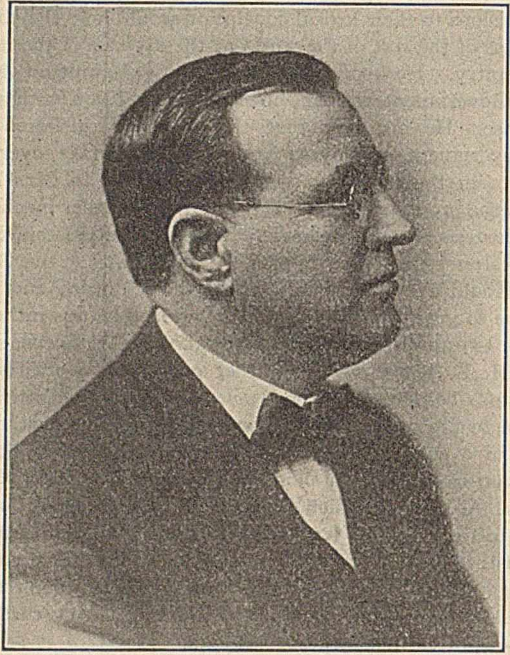
Dr. Rogers was born in Hampden, Maine, May 22, 1876, and graduated from the University of Maine in 1897 with the degree of B.S. in the chemistry course. For three years he remained at his Alma Mater as instructor in chemistry, receiving the M.S. degree in 1900. He continued his graduate work at the University of Pennsylvania and was awarded the Harrison Fellowship for 1901–2. In the latter year, the University conferred upon him its Ph.D. for a research concerned with certain complex inorganic acids, the results of which were published in the *Journal of the American Chemical Society*.

For two years longer he remained at the University, first as Senior Fellow, lecturing to graduate students on analytical and physical chemistry, and later as instructor in organic chemistry.

In June 1904 he entered the employ of the Oakes Manufacturing Co., Long Island City, N. Y., as research chemist, where his investigations on problems related to the leather industry led to several patents being taken out by the company.

[1] *J. Soc. Chem. Ind.*, **39** (1920), *9t*.

In September 1905 he returned to the ranks of the teachers, as professor in charge of industrial chemistry at Pratt Institute, Brooklyn, N. Y., the position he still occupies. Taking up his duties with characteristic energy and enthusiasm, he organized a course in industrial chemical engineering, making use of miniature plants to train young men for positions as foremen and superintendents in large-scale manufacturing establishments. This undertaking has been conspicuously successful from the outset, and already many of the graduates hold prominent places of great responsibility in our chemical industry.



Gardiner and Son

ALLEN ROGERS

Dr. Rogers is the author of the "Manual of Industrial Chemistry," in the preparation of which he was aided by over forty distinguished collaborators. This standard treatise has gone through three editions, and is now used as a text in more than fifty colleges and technical schools. He is also the author of "Elements of Industrial Chemistry" and "Laboratory Guide of Industrial Chemistry" (2 editions).

After this brief biographical account Professor Bogert said in part:

> For many years Dr. Rogers has made a special study of leathers and tanning, until he is now widely recognized as one of our foremost experts in this important field. Patents have been granted him for various processes of treating leather, and other patents are pending. His most interesting work in this direction is that recorded in the paper for which the medal is awarded, namely, the utilization of the shark and porpoise as sources of leather. In making the award, the Medal Committee entered upon their minutes a note expressing their judgment that Dr. Rogers' paper was a record of work accomplished by him in recovering oils, and manufacturing fertilizers and fine leathers, through which he contributed much information and some entirely new processes in applied chemistry.
>
> In the time of our country's need, he promptly and patriotically sacrificed all personal selfish interests and volunteered for military duty, being commissioned Major in the Chemical Warfare Service, where he was put in charge of the Industrial Relations Branch, a post of considerable responsibility, involving indirectly classification of industries into more and less essential, and determining recommendations of exemption from military duty for those chemists who were more needed at the factories than at the front. Many a plant would have had to close its doors, or seriously curtail its output, and the military preparation of the country would have been considerably delayed, but for the energy and ability with which Major Rogers fulfilled his duties. When the war had been won, he was equally active in aiding chemists discharged from the Army to get back into lucrative positions once more, an assistance which was deeply appreciated by many demobilized colleagues.

ABSTRACT FROM SPEECH OF ACCEPTANCE

By Allen Rogers

The commercial utilization of the shark is a matter that has interested me for several years and if I have done anything to interest others in my friends of the deep, it is, of course, very gratifying. Sharks have always been considered as scavengers, and of no benefit to man. My work, however, has shown me that they have some good points in their favor, and if we take advantage of them I feel confident that a great industry may eventually be established. Already much has been accomplished in this direction. A fairly large plant is in operation at Morehead City, N. C., where the fish are caught, the skins removed, the livers rendered for oil, and the flesh converted into fertilizer stock. Another plant is located at Sanibal Island, Fla.; and at the tannery in Newark, N. J., about one thousand skins are being treated each week. Plans are now under way for establishing other stations at various points along the Atlantic and Pacific Coasts, while the existing plants will be greatly enlarged.

CLEVELAND MEETING OF THE AMERICAN ELECTROCHEMICAL SOCIETY

The thirty-eighth meeting of the Society, its first in Cleveland, was held on September 30, and October 1 and 2, 1920. The attendance was smaller than expected, undoubtedly due to the greatly increased cost of travel. Those who came, some 175 visitors, were rewarded by fine papers and snappy discussions, interesting visits to laboratories and plants, and unexcelled social events and intercourse.

The Local Committee, under the direction of Dr. N. K. Chaney, of the National Carbon Co., aided by L. C. Drefahl, A. R. Bullock, and Mrs. E. R. Grasselli as heads of sub-committees, arranged visits to many of Cleveland's industrial plants, an afternoon at the Nela Park laboratories, and engaging diversions for the visiting ladies.

Among the papers read and discussed were the following: M. R. Wolfe and V. de Wysocki studied and measured the heat losses through the electrodes and their water-cooled rings, on a 6-ton Heroult steel furnace making steel castings, finding 123 kw. lost out of 650 kw. on the furnace, or 18.7 per cent of the power taken by the furnace. A. M. Kuhlman and A. D. Spillman measured the heat carried out of the same furnace by the steel and slag, making the heat content 476 to 520 cal. per kg. of slag, and 303 to 325 cal. per kg. of steel. M. L. Hartmann, A. P. Sullivan, and D. E. Allen, of the research laboratory of the Carborundum Co., reported measurements of the electrical resistivity of nine commercially used refractory materials, at temperatures which were slowly raised from cold to 1500° C. All showed great reduction, from nearly nonconductors when cold to below 10,000 ohms resistivity (per cm. cube) at 1500°; the actual values when 1500° was reached were

	Ohms per Cm. Cube
Bonded Carborundum (Carbofrax C)	8590
Silica Brick	8420
Magnesia Brick (Burned Magnesite)	2500
Bauxite Brick	1100
Fireclay Brick, Grade A	890
Bonded Carborundum (Carbofrax B)	745
Zirconia Brick (Natural Mineral)	412
Chrome Brick	41
Recrystallized Carborundum (Refrax)	1.6

The tremendous variations, of the order of 5000 to 1, point to interesting applications of this information to electric furnace work. It was pointed out in the discussion, however, that these resistivities are considerably changed by keeping the materials several hours at 1500°, sometimes being reduced 75 per cent, and that the final values obtained as constants on long heating are the quantities greatly desired.

F. A. J. Fitzgerald and G. C. Moyer noted the deterioration of nickel resistors in electric furnaces due to the absorption of sulfur. J. Kelleher spoke of curious flaring of the arcs observed in electric furnaces, making the observations through a pinhole diaphragm. Oscillograph records were also taken, while automatic current regulators were employed. The "arc" is found to consist normally of a set of small arcs around the periphery of the electrode; when the electrode approaches too near the slag, a large arc also appears, which is broken as the regulators raise the electrode, leaving only the small arcs working on a small portion of the electrode. This cuts down the current, and the regulators begin to lower the electrode. When the electrode almost reaches the slag, the small arcs suddenly spread over the whole end of the electrode, the current is largely increased, and the cycle of events described is repeated.

E. S. Bardwell described electric smelting of manganese ores at Great Falls, Montana, with a balance sheet of the heat distribution in the furnace which showed some 72 per cent of the electric energy usefully applied. The losses in the slags were large, one slag having nearly 20 per cent of manganese. It was pointed out in the discussion that the manganese losses in the slags varied in all cases inversely as the sum of Al_2O_3, CaO, and MgO, so that they were directly controllable by controlling the slag composition.

J. W. Richards described the first American installation of the Söderberg continuous self-baking electrode. This consists of three 32-in. round electrodes, used three-phase, in a 2000 kw. ferromanganese furnace at the plant of the Southern Manganese Corporation at Anniston, Alabama. These have worked continuously during July and August, the stoppages in 28 days in August on account of the electrodes being only 13 min.; carbon electrode consumption 14 lbs. per 1000 kw.-hrs. In the discussion it was stated that a 37-in. electrode of this design is now working in South Africa, and that the Stavanger Steel Company in Norway is successfully using Söderberg electrodes on a 6-ton tilting Heroult furnace.

E. A. Keeler described the advantages of exact conductivity measurements upon solutions as a means of recording and controlling industrial processes. For example, a test weight of a sugar sample is added to a given volume of a salt solution of known conductivity, and the per cent of sugar is determined from the decreased conductivity of the solution. If the sugar is already in solution, a fixed weight of salt is added to a fixed volume of the solution, and the conductivity measured.

C. J. Rodman and T. Spooner described a new, portable laboratory standard cell, in which a compact, concentric form is substituted for the familiar H type. Tungsten wire leads are used, and some particular methods of purifying the cadmium and its salts devised. Constancy to within 0.0001 volt in over two years is attained.

J. W. Richards called into question the direct relationship of electric current to electrochemical action at the cathode. At the anode the anion is of invariable valency, and a constant relation seems to subsist between the electrical current and the amount of anion liberated. It is to be noted that present electrical theory postulates negative electrons passing to the anode as the fundamental conception of the flow of electric current. At the cathode, varying amounts of the cation may be liberated, according to its varying valency, and the question is therefore asked, whether the amount of cation liberated is not determined *chemically*, as that amount which was united with the quantity of anion liberated, rather than fundamentally or primarily by an electrical relation. In the absence of definite proof of the existence of positive electrons, or, let us say, in the presence of a unitary theory of electrical current flow, the question is not without justification.

The session of Saturday morning was largely concerned with electroplating and metal refining. A. L. Ferguson and E. G. Sturdevant described investigations of the deposition of brass from cyanide solutions, accompanied by careful measurements of the potential and the effects of various additions. F. C. Mathers and W. H. Bell described negative results in the use of addition agents in plating tin from alkaline solutions. E. F. Kern described the electrolytic refining of tin, getting best results with stannous sulfate baths acidulated with 7 per cent H_2SO_4, and with the addition of peptone or gelatin. F. C. Mathers showed that gums, resins, or oleic acid are satisfactory addition agents to prevent the crystallization of lead depositing from alkaline electrolytes.

F. W. Skirrow and E. R. Stein described the production of hydrogen peroxide by electrolyzing potassium acid sulfate solutions with platinum anodes, crystallizing out the potassium persulfate formed, and distilling the crystals with sulfuric acid and water. A good yield of hydrogen peroxide is thus obtained.

E. A. Richardson and L. T. Richardson showed as the result of long-duration, air corrosion tests that the presence of copper reduces the corrodibility of pure iron and, to a greater extent, that of steel. In the case of steel, they suspect the manganese present to enhance the effect of the copper; this conclusion was called in question in the discussion, it being maintained that manganese had the opposite effect. The authors also stated that chromium had a still greater effect in reinforcing the protective action of copper. This conclusion was not disputed, since stainless steels prove the strong protective action of chromium.

W. D. Richardson of Chicago, in a paper of 34 pages, discussed the details of the solution of metals in acids as related to their corrodibility. In view of the use of accelerated tests to determine the resistance of metals to atmospheric corrosion, these tests are of importance. The principal point brought out was the great importance of various catalytic bodies, which are often present, in facilitating or retarding solution in acids. The influence of other factors, such as that of hydrogen, oxygen, carbon dioxide, halogens, and cathodic action, were also investigated.

All the papers had been printed in advance and distributed to members of the Society before the meeting. As a consequence discussions were lively and intelligent, and contributed discussion from a distance was frequently submitted. This has proved to be a highly successful method of bringing about a high-class scientific meeting.

A referendum of the Society as to making the metric system the exclusive legal system of weights and measures of the United States showed 483 in favor to 107 against. A majority of the members present did not favor increasing the annual dues by $1.50 in order that the Society might join the Federated American Engineering Societies. J. W. Richards

Lehigh University
South Bethlehem, Pa.
October 11, 1920

CALENDAR OF MEETINGS

American Petroleum Institute—Annual Meeting, Washington, D. C., November 17, 18, and 19, 1920.

American Institute of Chemical Engineers—Winter Meeting, St. Charles Hotel, New Orleans, La., December 6 to 9, 1920.

American Association for the Advancement of Science—Annual Meeting, Chicago, Ill., December 27, 1920, to January 1, 1921.

American Ceramic Society—Annual Meeting, Deschler Hotel, Columbus, Ohio, February 21 to 26, 1921.

American Chemical Society—Sixty-first Meeting, Rochester, N. Y., April 26 to 29, 1921.

NOTES AND CORRESPONDENCE

REPORT OF E. S. CHAPIN, PARIS REPRESENTATIVE OF THE TEXTILE ALLIANCE, INC., TO THE DYE ADVISORY COMMITTEE OF THE STATE DEPARTMENT, SEPTEMBER 29, 1920

I will divide the report into four parts: first, the Herty Option colors; second, the Reparation colors from the impounded stocks; third, German daily production and the future; and fourth, general comments.

HERTY OPTION

The orders placed with the Cartel by the Textile Alliance from assignments to them of licenses under the first six months' allocation amounted to 1,700,000 lbs. Up to September 7 the Cartel had delivered or were preparing to ship 1,200,000 lbs., approximately 70 per cent of the total orders. Of this, 374,000 lbs. have been shipped from Reparation sources; and 800,000 lbs., or 400 tons, have been shipped under the Herty Option. There have been 124,000 lbs. of cancellations, about 7 per cent of the total orders, leaving 397,000 lbs., that is, about 23 per cent, still to be delivered.

Orders placed were divided into vats and non-vats; 460,000 lbs. of vats and 1,240,000 lbs. of non-vats. The vat color orders are of especial interest. Of these 83 per cent have been delivered. The cancellations of vat colors were practically negligible, *i. e.*, only 3,000 lbs., or about two-thirds of 1 per cent. Of the 385,000 lbs. of vat colors delivered, 134,000 lbs. have come from Reparation and 251,000 lbs. have been shipped under the Herty Option.

The most notable aspect of the delivery of colors under the Herty Option is the change in the attitude of the Germans from apparent hostility to active coöperation with the Textile Alliance. In February and early March they had offered against this option the small sum of 192,000 lbs., and gave little promise or encouragement of being able speedily to deliver further quantities. In the last four or five months, however, they have been able to deliver an additional 600,000 lbs.

As regards the vat colors, in March they stated that they could deliver about 40,000 lbs. and held out no promise or encouragement of being able to ship large quantities in the future, but since then they have shipped 210,000 lbs.

The record of the Badische Company is especially interesting in connection with this change of attitude and improvement in performance by the Germans. This company received 43 per cent of the orders placed, that is, 732,000 out of 1,700,000 lbs.; and of the vat colors, 70 per cent of the orders, that is, 318,000 out of 460,000 lbs. To date, the Badische have delivered 625,000 lbs., that is, 85 per cent of their total orders, and of the vat colors they have delivered 280,000 lbs., or 89 per cent.

For months in letters and personal interviews various representatives of the Cartel have insisted upon the *bonne volonte* of the Cartel and their desire to do everything possible to coöperate with the Textile Alliance and to send their colors to the consumers in America.

Some comparisons are at times interesting and to the point. I was told by a British authority that Great Britain had secured on the free market up to August first, 200 tons of German dyes. This should be compared with our figure of 400 tons as of September 7, plus the unknown quantity imported into the United States under license through other channels. It is quite evident that the Cartel has made unusual efforts to send a large proportion of their free production to the United States. That they are anxious to sell to the United States came out quite strongly during my last trip to Germany. The representative of one of the factories asked me if they could not secure some more Herty Option orders. I was in Frankfort on September 1 when the Cartel was holding a special meeting, and had at that time several interviews with representatives of different factories in which they showed the greatest desire to coöperate

REPARATION COLORS FROM THE IMPOUNDED STOCKS

In the first place we must note that the impounded stocks were not so large in tonnage as was currently believed last fall. Erroneous information then placed the impounded stocks at 40,000 tons, of which one-half was to be divided among the Allies. As a matter of fact, the total of the August 15 inventory of impounded stocks was 20,000 tons, of which 50 per cent was to be distributed among the Allies. There were in the impounded stocks 13,000 different types of colors. The distribution of the impounded stocks among the Allies was made in two divisions: first, a division of 5200 tons, commonly known as the "5200 Ton" Agreement or the Protocol of November 4. According to this arrangement the different Allies were permitted to select certain colors not to exceed a certain percentage of each color and a certain gross tonnage; that is to say, the United States was allowed to choose 10.22 per cent of any color in the impounded stocks, not to exceed a gross tonnage of 1500 tons. France, for instance, was allowed to select 15 per cent of any color, not to exceed a thousand tons, etc. Great Britain had the same allocation as the United States.

The United States allocation of 1500 tons was taken in two different lots, known, respectively, as the 300-ton lot and the 1200-ton lot. The 300-ton lot included the 374,000 lbs., above mentioned as having been shipped against the first six months' allocation orders. It also included 76 tons of indigo 20 per cent paste, which were given by the United States representatives in Paris last winter to Belgium. The balance of the 1500 tons has been called the 1200-ton lot.

The cause of the division of the 1500 tons into two lots ordered at different periods was the method of providing payment. The Textile Alliance received, as is well known, the money for the 374,000 lbs. of reparation dyes applied against the first six months' allocation orders before placing orders with the Cartel; but for the balance of the 1500-ton lot had neither orders nor money. Further sound policy required that money must be in hand, or underwriting guarantees of payment, before the dyes should be ordered. In this emergency, in the interest of the United States and of American consumers, a few individuals, with the support of your Underwriting Committee, came forward and by providing underwriting saved the balance due the United States from the 5200-ton agreement.

The balance of the stocks was divided among the Allies according to a different system. The dyes were divided into 13 groups according to their nature, that is to say, whether Alizarin Red, vat color, indigo paste, direct cotton, or acid, and so on. These different classes were divided among the Allies according to different percentages, roughly corresponding to the needs for home consumption of the Allies. Thus the percentage of the United States for indigo paste was 5 per cent, because this product was not needed in the United States, whereas for Indanthrene Blue GCD, which was needed, the percentage was 55 per cent.

The second division, known as the Pool, that is to say, the balance of the impounded stocks, amounted roughly to 5000 tons. Here again we were confronted with the financial difficulty of the necessity of providing funds or underwriting before we could place orders for our allocated portion of dyes from the Pool; again the difficulty was solved by the underwriting already mentioned. The Pool contained many types in very small amounts and also many types and mixtures that it was not desirable to order. The gross of our orders after the New York office and the Paris office of the Textile Alliance had scanned the figures of the Pool amounted to approximately 500 tons.

To summarize, the total of our orders from the impounded Reparation stocks amounts to 2000 gross tons, or, to be exact, 4,435,635 lbs.

Of these 2000 tons, 100 tons have been applied to fill orders

100 tons of importable colors have been sold to consumers in the United States; 76 tons of indigo paste were given by our representatives in Paris last winter to Belgium, and 450 tons of indigo paste have been sold to China. The balance is about 1200 tons.

The Textile Alliance has rented a warehouse in Antwerp in which these 1200 tons are now stored or to which they are in process of shipment. Of the 1200 tons in the warehouse about one-half can be classed as colors that may be imported into the United States. We have thus approximately 600 tons of nonimportable colors.

Early realizing that the amount of nonimportable colors from the impounded stocks would be considerable, on my first trip to Germany in May I took up with the Frankfort people the matter of exchanging nonimportable colors for importable colors. At that time the answer was that they had nothing to give in exchange. On my last trip, however, I found a different state of affairs. The manufacture of the factories had increased considerably during the summer and there was a willingness to make trades. I have also taken up with our various Allies the matter of exchanging our nonimportable colors for importable colors and this is still in process of negotiation.

By securing all of the colors from the impounded stocks that were of value and to which the United States had the right, we have thus built up a reserve of products which can be used either directly for the benefit of the consumers of the United States or else indirectly by exchanging the nonimportables for the importables. After making all the exchanges possible of nonimportable for importable colors we are preparing to sell the balance of nonimportable colors.

I have already compared the 400 tons of dyes the United States has received under the Herty Option with the 200 tons received by Great Britain from the free market. In this matter of the shipment of Reparation dyes a brief statement of what our Allies have been doing will be interesting. The British found considerable difficulty in distributing the Reparation dyes allocated to them. Dr. Philippi, of the Cassella Color Company, made a trip to England in August in order to assist in facilitating the distribution and avoiding further delay. Last April, Herr von Weinberg and his secretary, Director Molner, made a trip to Italy, in the course of which they assisted the Italians similarly in distributing their dyes and avoiding the difficulties found in dealing with such a complicated matter. The French government distributed colors very actively among French consumers but nevertheless there was considerable complaint. Belgium's problems were simpler because of the small amount of colors received and they appear to have been dealt with quite successfully. None of the above-mentioned countries have had to contend with the most serious problems which faced the United States, namely, the Rotterdam strike and the distance from Germany.

GERMAN DAILY PRODUCTION AND THE FUTURE

The treaty provides that the Allies may exercise an option on 25 per cent of the daily production of the German factories for the period specified in the treaty. It further provides that in the event that this production is below the normal the Allies may require 25 per cent of the normal production.

The question of just what "normal production" means has not yet been settled by the Reparation Commission. In the meanwhile the commission has exercised this option and is accepting 25 per cent of the actual production of the German factories. This daily production it has been arranged to divide among the Allies very much in accordance with the scheme by which the Pool was divided among the Allies; that is to say, the different colors produced are divided into classes according to their nature, and divided among the Allies according to percentages corresponding approximately to the estimated needs of the various Allies.

During last winter the various Allies exercised very stringent supervision over the activities of the German factories. In order to break this control the Germans came forward in January and offered to supply all the needs of the Allies irrespective of the treaty stipulations, provided control was lifted from the factories. This proposition was accepted and in February and March the different Allies were busy in preparing a list of the requirements to be submitted to the Germans.

Our representatives were not in accord with the proposal, but as the French, Belgian, and Italian governments were insistent on their needs of dyestuffs and that the proposal should be accepted, our representatives did not feel that they could negative an offer on the part of the Germans to supply to the Allies all their requirements. Accordingly in May, after much discussion and many meetings, the lists of the requirements of the different Allies were forwarded to the Germans. This proved unacceptable to the Germans and this first proposal accordingly fell to the ground. Since then a new protocol has been drafted by the Dyestuff Bureau of the Reparation Commission. This new arrangement has not yet been discussed with the Germans and indeed has not yet been put into final shape by the Bureau. It is expected that the new protocol will be discussed by the various bodies of the Reparation Commission in late October and will be ready for discussion with the Germans in November.

In the meanwhile the Germans are putting aside 25 per cent of their daily production and this is allocated to the Allies in accordance with class and percentage. In order that the Allies may know what the Germans are making, on the fifteenth of each month the Germans submit a statement of the 25 per cent due the Allies from their production of the previous month. This includes every color produced, a statement of 25 per cent of the amount produced, and the price to the Allies, which according to the arrangement is the lowest price quoted during the month of production to any buyer, German or otherwise. A brief analysis of the quantitative and qualitative production of the German factories for the past six months will be of interest.

The total production of the German factories in the month of February, the first month for which a daily production list was submitted, was 1600 tons, approximately 10 per cent of their pre-war capacity. This production has steadily increased; 2400 tons in March, 3300 tons in April, 3800 tons in May, 4800 tons in June, and 5500 tons in July, or from approximately 10 per cent of their pre-war capacity in the course of six months to $33^1/_3$ per cent.

GENERAL COMMENTS

From the standpoint of the consumers of dyestuffs in the United States, this rapidly increasing production on the part of the German factories is not so satisfactory as might at first appear, for a large part of the increase in production is not the Herty Option colors, the colors desired by the consumers in the United States, but the big bulk colors, the colors that are being made by American manufacturers.

Take the three months—May, June, and July. The total production by all the German factories of vat colors and fast alizarin colors, which are especially desired by consumers in the United States, was approximately 800 tons. During the same period the production of indigo 20 per cent paste, direct cotton colors, acid colors, and sulfur colors amounted to 8800 tons, that is to say, eleven times as much as the production of vat colors and fast alizarin colors.

Further, while the production of the vat and alizarin type dye is increasing slowly from 228 tons in May to 261 tons in June and 272 tons in July, the production of the type of dyes made in the United States is increasing by leaps and bounds, from 2400 tons in May to 2800 tons in June and 3800 tons in July. This large German production of dyes of the same type as are being made in the United States is evidence of the necessity of special protection for the American industry. The relatively small German production of dyes of the Herty Option type explains the 23 per cent of the first six months' allocation orders still to be delivered.

The question naturally arises whether the Germans cannot produce more of the special colors desired by the United States. The arrangement which is being considered by the Reparation Commission aims to effect this purpose. The Germans do not like the necessity of putting aside 25 per cent of every color which they make during the month for the Allies and especially dislike the necessity of holding this 25 per cent against future orders, more or less problematical. Accordingly the Germans are inclined to consider a permanent proposition which will do away with the necessity of their putting aside 25 per cent of their daily production. The future of the supply of German colors to the United States is linked up with this permanent proposal. According to all indications when I left Europe, it seemed almost certain that the permanent proposal would be adopted in the course of a few months.

ALLIED CHEMICAL AND DYE CORPORATION

The merger of the General Chemical, Barrett, National Aniline & Chemical, Solvay Process, and Semet-Solvay Companies has been approved by the boards of directors of the companies concerned and the question of ratification is now before the stockholders.

The formal announcement by the stockholders' committee stated:

> * * * * * that the boards of directors of the respective companies have approved the plan of consolidation of the General Chemical Company, the Solvay Process Company, the Semet-Solvay Company, The Barrett Company, and the National Aniline & Chemical Company, Inc. Copies of the plan and deposit agreement will be mailed to stockholders as promptly as practicable.
>
> The name of the new corporation will be the Allied Chemical and Dye Corporation.
>
> The authorized capital stock will not exceed $65,000,000 7 per cent cumulative preferred stock, shares $100 par value, and 3,000,000 shares of common stock without par value.
>
> It is estimated that the outstanding capitalization of the new company, based on the deposit of all outstanding stock of the consolidating companies and after elimination of intercompany holdings, will be: Bonded indebtedness of consolidating companies undisturbed $9,493,000; 7 per cent cumulative preferred stock, $39,374,300; common stock without nominal or par value, 2,119,677 shares.
>
> If current earnings should be substantially maintained, as the committee believes they will be, and if substantially half of such earnings in excess of preferred dividend requirements should be distributed in regular quarterly cash dividends on the common stock of the new company, as the committee would favor, holders of such common stock may expect to receive regular quarterly cash dividends thereon at the rate of $6 per share per annum.
>
> The committee of stockholders of the consolidating companies in charge of the consolidation will be composed of the following gentlemen, who have been designated for that purpose by the boards of the respective companies:
>
> WILLIAM H. NICHOLS, chairman of the board of the General Chemical Company
> W. H. NICHOLS, JR., president of the board of the General Chemical Company
> E. L. PIERCE, president of the Solvay Process Company
> R. W. SWIFT, treasurer of the Solvay Process Company
> H. H. S. HANDY, president of the Semet-Solvay Company
> A. W. HUDSON, vice president of Semet-Solvay Company
> EVERSLEY CHILDS, chairman of the board of The Barrett Company
> W. HAMLIN CHILDS, president of The Barrett Company
> ORLANDO F. WEBER, chairman of the board and president of National Aniline & Chemical Company, Inc.
> WM. J. MATHESON, director National Aniline & Chemical Company, Inc.

Dr. Wm. H. Nichols is chairman of the committee, and Clinton S. Lutkins, 25 Broad Street, is the secretary.

The Guaranty Trust Company will be the depositary for all classes of securities and will issue transferable deposit certificates against deposits of stock under the plan. The Bankers Trust Company will act as the registrar of deposit certificates.

"CRIPPLING A GREAT WORK"

THE KNY-SCHEERER CORPORATION
OF AMERICA
NEW YORK

Oct. 6th, 1920.
In your reply refer to: N. E. F.

Journal of Industrial & Engineering Chemistry,
Room 343, No. 1 Madison Ave.,
New York City.

GENTLEMEN:

Our attention has just been called to an editorial appearing in your September number, under the heading, "Crippling a Great Work."

The reputation of your Publication prevents the thought that this article was written by you in a spirit of malice. No doubt the author who prompted the article, and whose patriotism has been heralded through the trade as "———'s Patriotism Pays," took advantage of your good nature and had the article written and published by you. An article of this kind can only be written and published with a view of injury to the party in question; so far as the general public is concerned, they are not interested.

The Kny-Scheerer Corporation of America is owned and controlled solely by born Americans; men who lent their services in many ways to their Government during the recent great struggle, and who did not measure their patriotism by the dollar-mark.

We feel that you believe in a square deal, and think that you will agree with us that in the article above referred to, we have not been treated fairly or squarely; and that your reputation for fair play will prompt you to extend to us the same courtesy that you would want extended to yourselves under similar circumstances.

This letter is written without feeling or resentment on our part as against your Publication, and we trust that you will receive it in the same spirit.

Yours very truly,
THE KNY-SCHEERER CORPORATION OF AMERICA
(Signed) N. E. FRANKLIN
President

FRANKLIN FILTER PAPER

To the Editor of
"The Journal of Industrial and Engineering Chemistry"
N. Y. City.

MY DEAR DR. HERTY:

Permit me to correct some erroneous statements published on page 955 of the Journal in reference to the "Franklin Filter Papers" which caused so much unpleasantness at the recent Chemical Exposition.

First of all, this line of filterpapers, manufactured by Messrs. Macherey, Nagel & Co., Dueren, who are represented in this country by myself, had been broadly advertised as German manufacture for at least 6 months previous to the exposition, and I feel certain that nobody ever intended to sell this paper under false pretense. Chemically treated paper for accurate gravimetric analysis is not being manufactured in this country, and the only other paper of this kind shown at the exposition was made in France and in England. Therefore, we have all reasons to believe that the parties who happened to be under the entirely mistaken impression that the German papers shown were offered as American manufacture were not American manufacturers of such material—as these do not exist—, but we are sure that those parties started the trouble either for pure business reasons or for reasons of personal dislike against the exhibitor of the material. My careful investigation of the entire incident leads me to believe that the latter alone was the basis of the attack. It is very unfortunate indeed, that a young businessman can be influenced by personal feelings to such an extent as to willfully misrepresent the facts to the management of the exposition. Naturally, these people were not aware of the fact that the paper had been advertised broadcast as German manufacture. The entire unpleasant incident is so much more difficult to explain as the same young business man has been selling the identical line of filterpapers for years under the name of "Dr. Nagel's" filterpaper; evidently he promoted Mr. Nagel to the Ph.D., in order to sell larger quantities of the paper made by the firm of which Mr. Nagel happened to be sales manager, while Mr. Macherey was in charge of the technical end of manufacturing operations, having held the position of Chief Chemist of Schleicher & Schuell for many years.

This willful shifting of the brand of the filterpaper by the same party which was so upset about the present label under which the paper is being marketed brings me to the second part of my argument. The present label of this line of filterpapers, showing Benjamin Franklin's picture, has been designed by a most patriotic American who served as Lieutenant in the Chemical Warfare Service during the war and whose ancestors have been patriotic Americans for many more generations as [*sic*] those of the man who started the entire unpleasantness. The reason for the change of label was only the difficult pronounciation of the manufacturers name: Macherey, Nagel & Co. No other reason was in the mind of the man who conceived and carried out the idea of the Franklin label, and each advertisement and circular on this material published by my firm showed plainly that the material was manufactured in Germany.

As mentioned before, neither the management of the exposition nor the editorial staff of the Journal was aware of these facts, but were willfully misled by a man who evidently let his personal feelings run away with his brains.

Yours very truly
(Signed) Herman A. Holz,
President,
Holz & Company, Inc.

P. O. Box 152,
Madison Square Station,
New York, N. Y.
October 14th, 1920

PLATINUM THEFT

President D. R. Anderson, of Randolph-Macon Woman's College, Lynchburg, Va., reports that its supply of platinum, amounting to 682.579 g., has recently been stolen.

WASHINGTON LETTER

By J. B. McDonnell, Union Trust Building, Washington, D. C.

INDUSTRIAL ALCOHOL

Establishment of an Industrial Alcohol and Chemical Division of the prohibition unit of the Bureau of Internal Revenue, effective October 15, has been announced.

Work heretofore assigned to the Division of Technology will be subdivided and administered by the Industrial Alcohol and Chemical Division and a new division to be known as the Permit Division, and the title of Division of Technology will be discontinued. Dr. A. B. Adams, former head of the Division of Technology, has been appointed head of the Permit Division, and J. M. Doran, assistant head of the old Division of Technology, has been made head of the Industrial Alcohol and Chemical Division. The Bureau's announcement stated that

> The change is made necessary by the increase in the work devolving upon the Division of Technology. The Permit Division will examine and pass upon applications for the manufacture of alcoholic products; determine all nonbeverage uses of intoxicating liquors and limitations of such uses; fix standards for manufactured articles containing alcohol; examine bonds; conduct trade investigations to determine whether products are bona fide and whether permitted articles are manufactured in accordance with approved formulas. The Industrial Alcohol and Chemical Division will have supervision of the construction and operation of industrial alcohol and denaturing plants, and control of the work of the plant officers; develop uses of denatured alcohol by laboratory work and research; examine denatured alcohol samples; examine samples of toilet articles, flavoring extracts, etc., and report the result of analysis to the Permit Division.

Establishment of a separate division in the prohibition unit of the Internal Revenue Bureau was urged upon officials some months ago by a large number of manufacturers and users of industrial alcohol at a conference held here. The situation in which the industry found itself at that time, because of the ofttime ridiculously hampering restrictions placed upon it by the prohibition forces, was made clear. Action on the request of the producers and consumers was necessarily delayed because of the illness of Commissioner of Internal Revenue Williams. While for the most part the executive officials in charge of the work of the Bureau recognized the justice of the complaint of the industry and the real need for relief, it is understood that action probably would have been taken sooner but for the attitude of some of those directly in charge of the affected divisions of the prohibition unit. However, action finally has been taken apparently along the right lines, and there should result an end to the petty hamperings of a vital industry by executive officials in their enforcing of the purely prohibition sections of the law.

THE DYE CENSUS

Comparison of 1914 imports, and production in the United States of dyes by classes in 1917, 1918, and 1919, will be contained in the forthcoming census of dyes and coal-tar chemicals of the United States Tariff Commission and will make available for the first time valuable comparative information.

The table was prepared by A. R. Willis, and other members of the chemical staff of the Commission who have been at work on the census, for the purpose of placing dye statistics in a form that can be readily interpreted by the consumer. It has not yet been worked out to absolutely final figures, because of inability to get all reports affecting totals. Certain preliminary figures, however, are tabulated below.

Type of Dye	Per cent of Total Imports 1914	Per cent of Total Production 1917	1918	1919
Acid dyes	20.21	.....	.....	18
Basic dyes	6.53	.....	.....	7
Color lakes and spirit-soluble dyes	3.29	2.03	.....	3
Direct dyes	22.34	24.32	21.01	23
Mordant dyes	9.69	9.06	9.32	8
Sulfur dyes	15.35	33.91	40.53	27
Vat dyes (including indigo)	22.53	0.63	5.61	15

It should be pointed out, in the case of the vat dyes, that synthetic indigo formed a very large part of the total classed as vat dyes in the table in 1919. While synthetic indigo also was included in the 1914 import figures, this dye formed a larger proportion of the total vat dyes produced here in 1919 than in the 1914 imports.

Varying conditions and developments in the history of our dye needs and manufacturing ability, of course, affected the production of these various classes of dyestuffs. In general, these fluctuations were accounted for in the preliminary statement of the census made by Dr. Grinnell Jones, chief chemist of the Commission, in his address last month at the Exposition of Chemical Industries in New York City.[1]

Statistics now being gathered for publication will give considerably more details regarding our dye industry than have heretofore been available. The War Trade Board has begun compilation of statistics showing the total licenses granted for dye imports during the fiscal year ending with June last. While the licenses granted by the Board will not mean in all cases actual imports, they will give as accurate a statement of the needs and desires of American dye consumers as it is possible to obtain in the opinion of War Trade Board officials.

Preliminary figures show that licenses were granted, during the fiscal year ending with June last, for dye imports from Germany amounting to 3,500,000 lbs., while licenses granted for imports from non-enemy countries totaled approximately 8,000,000 lbs., the largest proportion of which came from Switzerland, imports of more than 5,000,000 lbs. being licensed by the Board from that country.

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[1] This Journal, **12** (1920), 959.

While these War Trade Board statistics would be valuable in themselves, their value will be further enhanced by the publication by the United States Tariff Commission of a census of dye imports during the same fiscal year, using the Norton 1914 import census as the basis. An interesting comparison will be afforded by these two censuses of imports. Such import statistics as are regularly collected and made public by the Government through the Bureau of Foreign and Domestic Commerce of the Department of Commerce do not approach the detail desired, and such statistics as the Commission proposes to publish are not elsewhere available.

While the Tariff Commission is being discussed it might be interesting to note that Commissioner Culbertson in a speech recently delivered before the Southern Tariff Congress at New Orleans declared that the development of the American dye industry "reads like a fairy tale" of achievement.

Dyes, of course, are far from entitled to occupy the center of the chemical stage at all times, but to an ordinary layman it is somewhat surprising to find that the Government is conducting experiments with dyes as a possible cure for tuberculosis, under the direction of Dr. McCoy of the Hygienic Laboratory. Dr. McCoy is working in coöperation with Dr. Paul Lewis, of the Phipps Institute, Philadelphia, who also is engaged in conducting experiments along this line.

FEDERAL TRADE COMMISSION COMPLAINTS

Recent complaints issued by the Federal Trade Commission include charges of bribery of employees by the United States Color & Chemical Co., Inc., Boston, Mass., and the Seymour Chemical Company and Alexander S. Mann, Providence, R. I., textile finishing materials.

NAVAL RESEARCH LABORATORY

Bids for the construction of a Naval Research Laboratory to be established at Bellvue, D. C., were opened recently by the Navy Department. Bids will be opened later for supplying of laboratory equipment which will be desired. The laboratory is for the purpose of testing and experimentation on ordnance and ordnance materials and supplies and other articles, and other naval uses calling for laboratory research. The laboratory is to be established out of an appropriation of $1,500,000 given by Congress in 1917. Because of the wording of the appropriation, some of this fund has been used for other purposes, so that there is now available about $1,000,000 for construction of the plant.

THE DYE BILL

While little or nothing is being done in Washington at present —for obvious reasons—by supporters of the dye bill, the bill retains the same parliamentary status at the coming session of Congress in December as when that body adjourned last session. There is no doubt but that strong efforts will be made to have definite action taken by the Senate at this session. It should be borne in mind, however, that, in case of failure of the measure to get final action by Congress, both Senate and House, before adjournment of next session, it will lose all advantage it now has as a bill already passed by the House, and will have to go over the same steps which it began so many months ago.

October 16, 1920

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Signs of scientific and industrial activity are beginning to reappear. The annual industrial exposition held at Lyons (the Lyons fair) has just opened. This covers a district important in the chemical industry.

Owing to its proximity to the Alps and the Cevennes, the region of Lyons is particularly fortunate in possessing numerous waterfalls. The chemical works accomplished a great deal during the war, and since that time have adapted their manufactures to new needs. The pyrite mines of Saint-Bel, which are in this district, produce annually 270,000 tons, thus providing also for the development of all the industries dependent on sulfuric acid.

Exhibits at the Lyons fair by the different firms of the region include notably fats, stearin, glycerol, and gelatin. One company alone produces monthly 150 tons of oleic acid, 30 tons of glycerol, and 1,000 tons of soap.

Also to be noted are tanning extracts and natural coloring matters, 100,000 tons of which are annually produced in the region.

All the large industries of the district which use illuminating gas are recovering the benzene from the gas, in order to provide raw materials for the manufacture of dyes. Considerable effort has been made along this line.

The production of dyes during the past year was 1391 tons in the Lyons district alone, while in 1913 all the French industries together produced only 1000 tons.

Mention should also be made of the exhibit of photographic and pharmaceutical products by the well-known scientists, MM. Auguste and Louis Lumière, and also of the active efforts in the manufacture of textiles and artificial silk.

Professor Grignard now occupies the chair of organic chemistry of the Faculty of Sciences at Lyons, and he is actively engaged in promoting the necessary liaison between science and industry.

NICKEL PLATING OF ALUMINIUM

The French Society of Civil Engineers has just held its opening meeting of the season. An interesting paper was presented by M. Léon Guillet, professor at the Conservatoire des Arts et Métiers, who discussed the problem of the nickel plating of aluminium. This is not a new question, but all the patents dealing with this subject have not given satisfactory results.

The problem is that of developing the use of aluminium for coatings and obtaining a metal which is not attacked by different liquids, particularly sea water.

Good results are not obtained with perfectly polished aluminium. Neither should there be a too pronounced scouring. M. Guillet has obtained excellent results by a cleaning with jets of sand under light pressure (600 g.), followed by a nickel plating of 0.06 mm., then a copper plating of 0.012 mm., and finally a second nickel plating of 0.06 mm., the nickel and copper plating being effected in baths by the ordinary procedure.

Pieces thus prepared have been perfectly successful. Tests of stamping, of folding, and of burnishing, as well as the action of caustic soda, have proved the good quality of the nickel plating obtained.

The process has not been patented, and M. Guillet is quite ready to give further explanation to those interested. His sole interest is only to facilitate and popularize the use of aluminium.

SUGAR

M. Paul Kestner has recently installed in Saint-Gaudens (Haute-Garonne) and in Belgium, in the region of the Sambre, two large factories for the sugar fields. In the factories he is preparing "whole" sugar.

This sugar is incompletely defecated, leaving in the juice certain nitrogenous products of the beet. These products have a food value and until now have been discarded in the residue and used as fertilizer.

The sugar obtained by M. Kestner is slightly brown in color and can be used in the manufacture of chocolate and candy.

ARMAND GAUTIER

Professor Armand Gautier, one of the deans of French chemistry, has recently died at the age of 83. To him is due the discovery of nitriles, carbylamines, and ptomaines. He studied also the normal state of arsenic in the human body, and opened the way to the medical application of arsenical derivatives. He also carried on investigations on mineral waters and petroleum.

October 7, 1920

INDUSTRIAL NOTES

Experiments conducted by the Bureau of Plant Industry of the U. S. Department of Agriculture have proved the superiority of European seed-flax varieties for the north-central states.

The University of Buffalo has received a gift of $400,000 for the erection of a chemistry building, as well as anonymous gifts of $250,000 towards endowment and a library building.

The War Department has announced the sale of the Old Hickory Powder Plant at Jacksonville, Tenn., to the Nashville Industrial Corporation for $3,505,000. The Government has reserved a large amount of space at the plant for the storage of smokeless powder and other materials, as well as powder-making machinery. The Government also retains possession of the numerous concrete foundations which will assure the nucleus of a smokeless powder plant for completion and use in time of national emergency.

The Chemical Club of Philadelphia was formed at a luncheon given October 11, 1920, by the chemical jobbers and manufacturers of the city, and definite plans for the organization were formulated. Weekly luncheons are planned for the purpose of forming closer business relations among the chemical trade.

The Borden Company of New York has contributed to Columbia University $10,000 to be added to the gift previously made by it for research in food chemistry and nutrition under the direction of Prof. Henry C. Sherman. Dr. A. C. Langmuir of the class of 1893 has contributed $100 to be applied toward needed equipment in the department of chemistry.

Fire at the Butterworth-Judson Corporation plant in Newark, N. J., on September 20, completely destroyed the *p*-nitroaniline unit. Specifications for the new plant have been prepared and production is expected to begin by the first of December.

An institute for chemical and physical research has been founded in Japan at a cost of half a million pounds, subscribed by persons engaged in industry and commerce in Tokyo, Yokohama, and other towns. An annual subsidy of £200,000 has been granted by the government, and the emperor has made a personal donation of £100,000.

The office of the Technical Association of the Pulp and Paper Industry has been moved from 18 E. 41st Street to 542 Fifth Ave., New York City. The new quarters will provide opportunity for minor laboratory work, including microscopical, chemical, and physical testing of paper and fibers.

The General Electric Company has contributed $30,000 to extend the investigations of the Committee on Fatigue Phenomena of Metals of the Division of Engineering of the National Research Council, to include work on 3 per cent and 3.5 per cent nickel steel. The Engineering Foundation Board a year ago made a grant of $15,000 yearly for two years for investigations in carbon steels, the experimental work to be done at the University of Illinois under the supervision of Prof. H. F. Moore.

The United States Gypsum Co., of Chicago, has begun the construction of a plant at Sweetwater, Texas, to cost $1,000,000.

The Compressed Carbonic Co., of Baltimore, has been organized with a capital of $1,020,000, to recover 2,000,000 lbs. of carbon dioxide annually, using waste gas of the U. S. Industrial Alcohol Company at Curtis Bay. The following officers have been elected: President, A. R. Ludlow, vice president of the Air Reduction Co.; vice president and general manager, George B. Cowper.

The Emporia Potassium Phosphate Company is being organized at Emporia, Va., by Californian chemical engineers who have been instrumental in establishing the potash industry in Nebraska, to manufacture fertilizer from feldspar and phosphate rock. The process consists in fusing a combination of feldspar, phosphate rock, and a soda flux, and if the industry is developed as planned it is expected to mean revolutionizing the fertilizer industry, and rendering this country absolutely independent of German potash supplies. The product will be potassium phosphate, with an analysis of 16 per cent phosphoric acid and 6 per cent potash.

The American Cellulose and Chemical Company is to erect a large plant at Amcelle, Md., for the manufacture of artificial silk. If present plans are carried out, this will be the largest of its kind in the world.

The Crop Protection Institute has been organized by a group of scientific investigators and representatives of industrial concerns, with the advice and assistance of the National Research Council, to make a series of thorough scientific studies of the crop pests themselves and the means for improving and standardizing the materials and appliances used in fighting them. The Board of Trustees of the Institute is composed of nine scientific men representing leading scientific organizations and four representatives of manufacturing and commercial interests, with H. E. Howe, chairman of the Division of Research Extension of the National Research Council, acting as temporary secretary. The Institute will not duplicate existing efforts of government bureaus, state experiment stations or other agencies, but will introduce a more general coöperation and give special attention to filling important gaps now existing.

Twenty chemical companies were organized during the month of September 1920, with a total capitalization of $7,720,000, as compared with $36,715,000 in August and $21,475,000 in July. The total authorized capital of new companies for the first nine months of 1920 is $175,642,000 as compared with $77,436,000 in 1919, and is 50 per cent greater than the total during the year 1919.

The production of petroleum in the United States during 1919 showed an increase of about 6 per cent in quantity and 10 per cent in value over 1918, while natural gas showed a decrease of about 20 per cent in quantity.

2,000,000 tons of potash were imported to the United States from Germany in 1913, as compared with 92,000 tons for the first half of 1920.

A number of prominent steel foundries grouped for the purpose of developing and perfecting higher standards in the production of steel castings have appointed Mr. R. A. Bull, of Pittsburgh, as consulting metallurgist to devote his entire time to research work.

The manufacture of artificial fertilizer is becoming a major industry in Japan, although before the war there was only one company of any size engaged in its production. One handicap of the industry is the necessity of importing the raw materials.

The Fort Worth Acid Works, Fort Worth, Texas, is building a plant for the purpose of extracting sulfuric acid from the sludge of oil refineries. A large percentage of the acid used in the process of refining petroleum products remains in its original state, except for being rendered unavailable for further use through accumulation of particles of tar, asphalt, and other substances, but the amount of sludge from one refinery does not justify the installation of machinery for reclaiming. The Fort Worth Acid Works will obtain its raw material from refineries at Fort Worth, Dallas, Wichita Falls, Ranger, and other points.

The six-acre plant of the Barber Asphalt Company near Perth Amboy, N. J., was recently destroyed by fire with a loss of nearly $3,000,000. The four units of the plant for asphalt refining, for making roofing asphalt, for asphalt flooring products, and for asphalt paving blocks were burned, with their storehouses, only the piers along the waterfront escaping the fire. Two of the six steel tanks containing asphalt were also destroyed.

The National Malleable Castings Company has opened its new laboratory in Cleveland, Ohio, which is devoted purely to research and general investigations, the routine analytical and testing work required for works control being carried on at the various plant laboratories. The department occupies a three-story building which is equipped for work in chemistry, physics, metallography, metallurgy, and materials testing. H. A. Schwartz is manager of research, H. R. Payne, chief chemist and acting metallographer, M. M. Austin and Anna Nicholson, research chemists, A. F. Gorton, physicist, W. W. Flagle, engineer of tests, and C. A. Thornburg, chief clerk.

Experiments in the development of the turpentine industry in California during the winter season of 1919–20 have proved satisfactory. 10,000 cups were placed, and 39 bbls. of gum gathered and shipped to a refinery in San Francisco.

The Canadian Dominion Bureau of Statistics has recently issued a preliminary report in regard to the paint and varnish industry of Canada in 1918. During 1918, 45 plants were in operation, with total assets of $15,784,610, and raw materials costing $9,203,530 were used.

The United States Civil Service Commission has announced open competitive examinations for chemist at $3,000 to $5,000 a year, and associate chemist at $2,000 to $3,000 a year, to fill positions in the Chemical Warfare Service, Edgewood Arsenal, Edgewood, Md., and others requiring similar qualifications. Competitors will be rated on (1) education, training, and experience, (2) experience and training as an executive, and (3) original research work completed, and must qualify in at least one of the following optional subjects: Advanced inorganic chemistry, analytical chemistry, organic chemistry, pharmaceutical chemistry, and physical chemistry. Applications, together with unmounted photographs, must be filed by November 9, 1920, with the secretary of the Fourth Civil Service District, Old Land Office Building, Washington, D. C.

The Melbourne & Metropolitan Gas Co., of Australia, which carbonizes annually from 250,000 to 300,000 tons of coal, is considering plans for the installation of a distillation plant for the recovery of by-products of coal tar which are now wasted. The by-product plant of the Australian Gas Light Co., in Sydney, produces a revenue of $681,000 annually, treating only half of the 400,000 tons of coal used annually.

PERSONAL NOTES

Dr. Ellwood B. Spear has resigned from the faculty of the Massachusetts Institute of Technology to accept a position with the Goodyear Tire & Rubber Co., Akron, Ohio.

Mr. Robert F. Wood, for four years metallurgist with the Sandusky Foundry & Machine Co., Sandusky, O., has resigned from that position and has accepted a similar one with the Monel Metal Products Corp., Bayonne, N. J.

Mr. Harold O. Trotter who has been doing special detail work in St. Louis among physicians and dentists for Bristol-Myers Co., of Brooklyn, N. Y., is now connected with Eli Lilly & Co., Indianapolis, Ind., in their manufacturing division.

Mr. Winfield Scott has left the employ of the Goodyear Tire & Rubber Co., Akron, O., where he had charge of organic research, and has accepted a position with the Quaker City Rubber Co., Philadelphia, Pa., where he is in charge of the research department.

Mr. W. Vernon Godshall, formerly assistant professor of general, qualitative, organic, physiological and household chemistry at Miami University, Oxford, O., has accepted a similar position in physiological chemistry in the department of physiology of the University of Wisconsin, Madison, Wis., and also a position as chemist on the Interdepartmental Board for the estimation of the elimination of arsenic from patients treated with certain arsenical drugs in case of syphilis.

Mr. Max Albert, formerly chemist in charge of the branch chemical laboratory of the Bureau of Standards, Northampton, Pa., is now connected with the Newport Chemical Co. (Carrollville, Wis., operation) where he is engaged as research chemist, working on improved methods for manufacturing crystalline sodium sulfide (suitable for use in connection with production of sulfur dyes).

Mr. C. A. Browning, formerly head of the chemical department of Howe Military Academy, Howe, Ind., has recently taken a position with the People's Gas Light & Coke Co., of Chicago.

Mr. A. F. Wendler has resigned as instructor in chemical engineering at the University of Michigan, Ann Arbor, Mich., to accept a position in the test division of the engineering department of the National Aniline & Chemical Co., of Buffalo, N. Y.

Mr. Paul J. Peterson is now chief chemist with Wadsworth, Howland & Co., Malden, Mass., having formerly been connected with the North Dakota Agricultural College.

Mr. Alfred E. Galloway, a former graduate student and assistant in organic chemistry in the department of chemistry at Ohio State University, Columbus, O., has accepted a position in the organic research laboratory of the New Jersey plant of the Grasselli Chemical Company.

Mr. W. H. Keen resigned a short time ago from the Hess Steel Co., Baltimore, Md., where he held the position of tool steel manager, and has opened an office as consulting metallurgist in Newark, N. J.

Mr. P. J. Anderson has left the Root & Van Dervoort Engineering Co., East Moline, Wis., and has accepted a position with the Samson Tractor Co., Janesville, Wis., where he has charge of cupolas and mixing of grey iron and semi-steel.

Dr. Glenn S. Skinner, formerly assistant professor in organic chemistry at Oberlin College, Oberlin, O., has accepted a similar appointment in the department of chemistry at the University of Wisconsin, Madison, Wis.

Dr. G. R. Shaw, upon receiving the doctor's degree at the University of Wisconsin last June, left work there as an instructor and accepted a position with the experimental engineering laboratory of the National Lamp Works of the General Electric Co., Cleveland, Ohio.

Mr. James R. Wilson, formerly teaching fellow at the California Institute of Technology, Pasadena, Cal., is at present in the research department of the Western Electric Co., New York City.

Mr. Charles M. Hayes, a recent graduate from the Pennsylvania State College, is now connected with the National Carbon Co., Inc., Lakewood, Ohio, in the engineering department of their American Ever-Ready Works.

Mr. Harold Bedient, who has been an assistant in chemistry at Cornell University, where he was studying for his Ph.D. degree, sailed September 18 for China to take a position as professor of organic and sanitary chemistry in the Fukien University at Foo Chow, China.

Mr. Lloyd A. Hall resigned as chief chemist with John Morrell & Co., Ottumwa, Ia., to accept a similar position with the Boyer Chemical Laboratory Co., Chicago, Ill.

Dr. Edward Culmann, formerly with the Schoellkopf Works of the National Aniline & Chemical Co., Buffalo, N. Y., is now connected with the American Aniline Products, Inc., as technical director of the Lock Haven Works, Lock Haven, Pa.

Mr. Raymond E. Kirk resigned as instructor in the department of chemistry, Iowa State College, Ames, Ia., and entered upon his duties as assistant professor of general inorganic chemistry in the School of Chemistry of the University of Minnesota, Minneapolis, Minn.

Recent additions to the personnel of the Research Division, C. W. S., at Edgewood Arsenal, which is being increased rapidly to take care of the many problems which come to this Division, are as follows: **Messrs. John C. Bubb, T. E. Knapp, K. D. Ashley, Earl H. Barclay,** and **W. L. Tanner**, research chemists; **Messrs. V. T. Ellis,** and **H. L. Humphrey**, chemical engineers; **Messrs. J. C. Goshorn, Earl Otto, Benjamin Engleman, Max Berlin, J. D. Craig, E. M. Berry, H. E. Bloomsburg, R. S. Brown, Mark C. Lewis, Philip Barnhart,** and **T. E. Kendrick**, junior chemists, and **Mr. E. K. Long**, mechanical and electrical engineer. It is expected to increase the chemical and mechanical force until Edgewood has between 200 and 300 technical men engaged upon research, plant development, smoke and incendiary development, and toxicological work.

A laboratory for research on dyestuffs and explosives has been established at George Washington University, Washington, D. C., under the general supervision of **Prof. H. C. McNeil**, and in charge of **Mr. G. W. Phillips**, formerly of the Chemical Warfare Service. **Dr. C. E. Monroe**, of the National Research Council, will be consulting chemist of the laboratory.

Mr. Olin K. Smith has left the Federal System of Bakeries of America and has taken a position as industrial engineer with the Western States Portland Cement Co., of Independence, Kans.

Mr. F. H. Fish, formerly special research test assistant on the joint investigation of the fatigue of metals at the University of Illinois, Urbana, Ill., has been appointed associate professor of analytical chemistry in the Agricultural and Mechanical College of Texas, College Station, Texas.

Mr. R. H. Bullard has resigned his position with the Roessler & Hasslacher Chemical Company in order to return to Hobart College, Geneva, N. Y., as instructor in chemistry.

Mr. C. J. Overmyer, Rhodes Scholar from Michigan as of 1919, left the chemistry department of Michigan Agricultural College, East Lansing, where he was an instructor, and has sailed for Oxford, England, where he will enter Oriel College for three years' work in chemistry.

Mr. W. G. Bowers, having resigned as head of the laboratory of the State Food Commission, Fargo, N. D., recently accepted an appointment as head of the department of chemistry in the Colorado State Teachers' College at Greeley, Col.

Mr. H. H. Brown, formerly connected with the Bureau of Chemistry, Department of Agriculture, where he was in charge of the chemical investigations on the cause and prevention of dust explosions, is at present employed by the Pejepscot Paper Co., Brunswick, Maine, to establish a chemical research laboratory and to investigate chemical problems connected with the manufacture of paper and the utilization of waste products.

Mr. L. D. Vorce resigned as works manager with the Canadian Salt Co., to take up active duties with the Precision Instrument Co., of Newark, N. J., of which concern he is vice president.

Mr. W. W. Hambly, until recently connected with E. I. du Pont de Nemours & Co., has secured a position in the production department of the General Electric Co., Schenectady, N. Y.

Mr. R. B. Arnold has given up his work as consulting chemical engineer at Richmond, Va., and has become vice president, in charge of manufacture, of the Delion Tire & Rubber Co., of Baltimore, Md.

Mr. Ralph B. Hammond, formerly research chemist at the Mathieson Alkali Works, Inc., Niagara Falls, N. Y., has resigned from that position to become division superintendent of the Acheson Graphite Company, of the same city.

Mr. H. B. Pulsifer, formerly of the Montana State School of Mines, is now assistant professor of metallurgy at Lehigh University, Bethlehem, Pa.

Mr. George D. Chamberlain recently changed his business connections from metallurgical engineer for the Heppenstall Forge & Knife Co., Pittsburgh, Pa., to assistant general superintendent of the Standard Seamless Tube Co., Ambridge, Pa.

Mr. Lauren H. Ashe has resigned as chief chemist and production manager of the Capital City Products Co., Columbus, Ohio, to become assistant general manager of the Ko-Ko-Mar Co., of Cleveland, Ohio.

Mr. Chas. L. Wiswall recently accepted a position with the Perth Amboy Chemical Works, Perth Amboy, N. J., as chemical engineer, his former position being production manager of the Vulcan Detinning Co., Sewaren, N. J.

Mr. E. B. Cordon upon graduating from the University of North Carolina last June accepted a position as a chemist in the plant laboratories of the Pratt and Lambert Varnish Co., Buffalo, N. Y.

Dr. Waldemar T. Schaller has severed his connection with the Great Southern Sulphur Co., Inc., of New Orleans, La., and has returned to the U. S. Geological Survey, Washington, D. C.

Mr. Fred S. Mulock, formerly operating superintendent of the U. S. Bureau of Mines at the U. S. Government Experiment Station, Petrolia, Texas, is now in the research department of the U. S. Smelting, Refining, and Mining Co., Boston, Mass., and is at the same time connected with the U. S. Bureau of Mines as consulting mechanical engineer.

Dr. M. C. Teague resigned as gas chemist at the Pittsburgh Station of the U. S. Bureau of Mines to accept the position as research chemist for the U. S. Rubber Co., New York City.

Mr. Paul D. Watson, a graduate last June in the chemical engineering course at the University of Pittsburgh, is now assistant chemist with the General Chemical Co., at their Laurel Hill Laboratories, L. I., N. Y.

Mr. M. C. Burt, formerly connected with the Aetna Explosive Co., has been put in charge of the Bridgeport Works of the Remington Typewriter Co., Bridgeport, Conn., where carbon paper and typewriter ribbons are manufactured.

Mr. Reginald K. Pierce,, treasurer of the Semet-Solvay and the Kentucky Solvay companies, was killed recently in an automobile accident.

Mr. Harry I. Johnson has been appointed director of the new chemistry department at Roanoke College, Salem, Va., having resigned as assistant professor of chemistry at N. C. State College of Agricultural & Engineering, West Raleigh, N. C.

Mr. Ralph A. Gould and **Mr. Bryant S. Drake** announce their association from August 1, 1920, as a partnership under the firm name of Gould & Drake, chemical engineers, with offices in San Francisco, Cal.

Mr. Thomas P. Shields has left Hoover & Strong, Inc., Buffalo, N. Y., where he was superintendent, to take a position as technical director of Wendall & Co., manufacturing jewelers and refiners, New York City.

Dr. Roland Neal, professor of chemistry at the College of the Pacific, San Jose, Cal., since 1910, has been appointed to the professorship of chemistry in Drury College at Springfield, Mo.

Mr. Thomas E. Comerford, formerly employed as chemist by the Aetna Explosive Co., at their Fayville, Ill., plant, is at present employed in a similar capacity by the Oldbury Electrochemical Co., Niagara Falls, N. Y.

Mr. Fred W. Geise, for the past three years connected with the U. S. Department of Agriculture, Bureau of Plant Industry, Washington, D. C., with temporary station at University of Chicago, Hull Botanical Laboratories, Chicago, Ill., is now associate plant physiologist with the Virginia Truck Experiment Station, Norfolk, Va.

Mr. C. H. Kidwell resigned recently as chief of the Quality of Water Division of the Water Resources Branch of the U. S. Geological Survey, Washington, D. C., to accept a position with the Solvay Process Co., Syracuse, N. Y.

Mr. Robert H. Currie, formerly of the main office chemical staff of the du Pont Co., Wilmington, Del., has accepted a position with the Acheson Graphite Co., Niagara Falls, N. Y., as superintendent of the lubricant works.

Mr. Claude E. McLean resigned his position as first assistant chemist in the Memphis Laboratory of the Union Seed & Fertilizer Co., to accept a position as chemist in charge of a laboratory for the Osage Cotton Oil Co., Muskogee, Okla.

Mr. H. B. Corbett has severed his connections with the U. S. Public Health Service as sanitary bacteriologist, and has joined the forces of the H. A. Metz Laboratories, New York City, where he will work in the biological testing division.

Mr. Paul Moore, now director of the Information Bureau of the War Trade Board, became Secretary of the Division of Research Extension, National Research Council, on or about October 1, and will devote his efforts to the promotion of research with special reference to the industries.

Mr. Carl G. Hinrichs, a graduate of the St. Louis College of Pharmacy, has been elected associate professor of chemistry of that institution.

Dr. H. E. Wells, formerly professor of chemistry at Washington and Jefferson College and a Captain in the Chemical Warfare Service, U. S. A., has been appointed professor of chemistry at Smith College, Northampton, Mass.

Mr. F. H. Tucker has severed his relations as associate chemist of the Bureau of Standards, Washington, D. C., to become chemist in the research laboratories of the Chile Exploration Co., New York City.

Mr. Geoff A. Saeger resigned as chief chemist for the Lehigh Portland Cement Co., New Castle, Pa., to accept a similar position with the Bessemer Limestone & Cement Co., Bessemer, Pa.

Mr. Benjamin R. Jacobs recently announced his resignation from the Bureau of Chemistry, Washington, D. C., having accepted the directorship of the National Cereal Products Laboratories, with offices in the above city.

Dr. F. Hastings Smyth resigned as secretary of the Clinton Metallic Paint Co., Clinton, N. Y., to accept a position on the staff of the Geophysical Laboratory of the Carnegie Institution of Washington.

Mr. F. D. Haskins who was formerly instructor in chemistry at Washington University, St. Louis, Mo., has been appointed assistant professor of chemistry at Mercer University, Macon, Ga.

Mr. G. H. Montillon, instructor of chemical engineering at the University of Wisconsin, Madison, Wis., for the year 1919–1920, has resigned, and is now assistant professor of chemical engineering at the University of Minnesota, Minneapolis, Minn.

Dr. Arthur M. Buswell, formerly instructor in sanitary chemistry at Columbia University, has been appointed chief of the Illinois State Water Survey, and associate professor in sanitary chemistry at the University of Illinois.

Dr. Carl L. Alsberg, chief of the Bureau of Chemistry, was elected president of the Association of American Dairy Food and Drug Officials at their recent convention held in St. Louis.

Mr. Charles W. Cuno, formerly professor of chemistry at Yankton College, Yankton, S. D., has accepted the position of assistant professor of chemistry in Washington University, St. Louis, Mo.

Mr. C. W. Botkin, associate professor of chemistry at the Colorado School of Mines, has resigned to accept a position as research chemist for the American Shale & Petroleum Co., of San Francisco, Cal. The research work, however, will be conducted at the Colorado School of Mines in Golden, Col.

Mr. Harold N. Hermann recently joined the engineering staff of the Mantius Engineering Co., Inc., New York City, having previously been associated with the Eflorose Sugar Co., Carthage, Ohio, as chemist.

Mr. H. B. Riffenburg, assistant professor of chemistry and chemical engineering, at Texas Agricultural and Mechanical College, College Station, Texas, recently resigned to accept a position as junior chemist in the Quality of Water Division of the Water Resources Branch of the U. S. Geological Survey, Washington, D. C.

Mr. R. A. Watson, formerly with the Gem Yarn & Dye Works of Central Falls, R. I., has become teacher of dyeing in the Philadelphia Textile School, Philadelphia, Pa.

Mr. Raymond A. Heindl has resigned as assistant chemist with the Aluminum Company of America to accept the position of chemist with the National Abrasive Co., Niagara Falls, N. Y.

Dr. Rodney B. Harvey resigned as plant physiologist, Bureau of Plant Industry, Washington, D. C., to accept the position of assistant professor in plant physiology at the University of Minnesota, and assistant plant physiologist in the Minnesota Experiment Station. Dr. Harvey will still be retained by the Bureau of Plant Industry as collaborator under a coöperative arrangement.

Mr. John F. McBride who was formerly in the research department of the National Aniline & Chemical Co., studying methods of production of certain dyestuffs and intermediates, has entered the department of chemistry of the University of Chicago where he will begin research for the Ph.D. degree in organic chemistry.

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. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

UNITED STATES TARIFF COMMISSION

Barytes, Barium Chemical, and Lithopone Industries Including Costs of Production, 1919. Tariff Information Series No. 18. 90 pp. Paper, 15 cents. Issued September 1920.

The Crude Botanical Drug Industry. Tariff Information Series No. 19. 69 pp. Paper, 10 cents. Issued September 1920. This pamphlet presents a discussion of the crude botanical drug industry, with special reference to those foreign and domestic articles of chief importance in the drug trade. The report is divided into two parts and an appendix. (1) Drugs are defined and classified, and the world trade, production, and consumption of these articles are discussed; a brief review of tariff treatment and policy is also presented. (2) This chapter classifies drugs according to their geographical source, and is chiefly concerned with the principal imported articles and those which have been or may probably be cultivated commercially in the United States. (Appendix.) The portions of the Tariff Act of 1913 referring to drug products are cited.

PUBLIC HEALTH SERVICE

Acid Burns on Hands of Solderers. Experience at the Curtis Bay General Ordnance Depot, South Baltimore, Md. H. W. Keatley. Public Health Reports, 35, 2161–3. The soldering process, the problem it presents, the causes of the burns, and preventive measures are described.

Methods of Increasing the Efficiency of Rural Sanitation. T. J. Robinson. Public Health Reports, 35, 2200–2.

"Fake" Orange Beverages. Public Health Reports, 35, 2204–5. Attention is called to the fact that these "fake" preparations are generally lacking in the organic acids and the vitamines which give medicinal value to the genuine orange juice.

The Effect of Shaking Alkalinized Aqueous Solutions of Arsphenamine and Aqueous Solutions of Neoarsphenamine in the Presence of Air. G. P. Roth. Public Health Reports, 35, 2205–10. Shaking alkalinized aqueous solutions of arsphenamine or aqueous solutions of neoarsphenamine in the presence of air renders them highly toxic, as shown by intravenous administration to white rats. The increase in toxicity caused by such shaking is presumably due to the oxidation of these compounds to *p*-oxyphenylarsenoxide, inasmuch as shaking a solution of neoarsphenamine in the absence of air does not increase the toxicity of such a solution. The conclusion drawn from the investigations is that the toxicity of aqueous solutions of neoarsphenamine is greatly influenced by the manner in which they are prepared for administration.

Quantitative Studies in Chemotherapy. I. The Trypanocidal Action of Arsenic and Antimony Compounds. Carl Voegtlin and H. W. Smith, with the coöperation of M. M. Crane, K. D. Wright and M. A. Connell. Public Health Reports, 35, 2264–73. A method for the rapid and accurate determination of the trypanocidal power of drugs is recommended. A sharply defined minimum effective dose is observed, below which the drug has no appreciable effect upon the parasites of infectious diseases. Arsphenamine and neoarsphenamine have to be oxidized in the body before they can act upon the parasites.

Treatment and Disposal of Sewage. Brief Descriptions of Methods, Processes, and Structures Used in the Treatment and Disposal of Sewage in the United States, with Bibliography. H. B. Hommon, J. K. Hoskins, H. W. Streeter, R. E. Tarbett and H. H. Wagenthals. Reprint No. 580 from Public Health Reports. 36 pp. Paper, 10 cents. 1920.

Prevention of Stream Pollution by Dye and Intermediate Wastes. E. J. Casselman. Reprint No. 581 from Public Health Reports. 23 pp. 1920.

GEOLOGICAL SURVEY

Mineral Resources of the United States in 1919. Preliminary Summary. Introduction by G. F. Loughlin. Statistics assembled by M. B. Clark. 128 pp. Issued September 8, 1920. Statistics of mineral production in the United States for 1919 reflect the reaction from intensive production for war purposes and the unsettled state of industry in general. Production of special "war minerals" rapidly subsided, although not to its pre-war status. The principal decline was due to diminished production of coal and the major metals. The total value of all mineral products in 1919 was about $4,653,700,000, 16 per cent less than in 1918. The value of metal products decreased 36 per cent, but it is estimated that the value of mineral fuels and other nonmetallic products decreased only 3 per cent due to higher prices in 1919. A comparison of production in 1913 and 1919 indicates an increase of 86 per cent in total value due to increase in price. With the exception of the "war minerals" most commodities were below normal in output. Marked increases in production are to be expected in 1921 and succeeding years until normal output is reached.

Cobalt, Molybdenum, Nickel, Titanium, Tungsten, Radium, Uranium, and Vanadium in 1917. F. L. Hess. Separate from Mineral Resources of the United States, 1917, Part I. 61 pp. Published August 31, 1920. The various metals are treated separately, with the exception of radium, uranium, and vanadium, which are handled as one group, and in nearly every instance general conditions, production, uses, prices, imports and exports are described.

Gold, Silver, Copper, Lead, and Zinc in Colorado in 1918. C. W. Henderson. Mines Report. Separate from Mineral Resources of the United States, 1918, Part I. 57 pp. Published September 2, 1920. The total value of the gold, silver, copper, lead, and zinc produced in Colorado in 1918 was $34,160,172, a decrease of 19 per cent from the value in 1917.

Petroleum in 1918. E. R. Lloyd. Separate from Mineral Resources of the United States, 1918, Part II. 201 pp. Published September 20, 1920. The year 1918 witnessed the organization of the industry on a war basis under the direction of the United States Fuel Administration, a quickening of activity in all phases of the industry, and an active coördination of all its branches in a complete and unified organization for the one purpose of supplying petroleum products for the necessary operations of the United States and the allied nations in winning the war. The one region of outstanding interest was northern central Texas. The quantity of crude petroleum produced in the United States in 1918 aggregated 355,927,716 bbls. of 42 gal. each, an increase of more than 6 per cent over the former maximum yield of 335,315,601 bbls. in 1917.

Natural-Gas Gasoline in 1918. E. G. Sievers. Separate from Mineral Resources of the United States, 1918, Part II. 35 pp. Published September 22, 1920. The quantity of natural-gas gasoline produced in 1918 was about 30 per cent greater than that produced in 1917; the increase in 1917 over 1916 was 110.5 per cent. The total quantity of raw gasoline recovered in 1918 was 282,535,550 gal. The outstanding feature of the industry in 1918 was the large increase in production by the compression plants in Oklahoma.

Arsenic, Bismuth, Selenium, and Tellurium in 1919. J. M. Hill. Separate from Mineral Resources of the United States, 1919, Part I. 9 pp. Published September 16, 1920. Statistics are given showing the production, imports, exports, and price of arsenic and bismuth. In the case of selenium, statistics showing the production, imports, consumption, and price are given. There was a small demand for tellurium in 1919, but the stocks of tellurium are apparently large as compared with the annual consumption.

A Deposit of Manganese Ore in Wyoming. E. L. Jones, Jr. Bulletin 715-C. Separate from Contributions to Economic Geology, 1920, Part I. 3 pp. Published September 18, 1920.

Some Deposits of Manganese Ore in Colorado. E. L. Jones, Jr. Bulletin 715-D. Separate from Contributions to Economic Geology, 1920, Part I. 12 pp. Published September 17, 1920.

Geology of the Yellow Pine Cinnabar-Mining District, Idaho. E. S. Larsen and D. C. Livingston. Prepared in coöperation with the Idaho State Bureau of Mines and Geology. Bulletin 715-E. Contributions to Economic Geology, 1920, Part I. 11 pp. Published September 15, 1920.

Deposits of Iron Ore near Stanford, Montana. L. G. Westgate. Bulletin 715-F. Contributions to Economic Geology, 1920, Part I. 8 pp. Published September 16, 1920.

Surface Water Supply of the United States, 1917. Part II. South Atlantic Slope and Eastern Gulf of Mexico Basins. N. C. Grover, G. C. Stevens, and W. E. Hall. Water-Supply Paper 452. 92 pp. Paper, 10 cents.

Surface Water Supply of the United States, 1918. Part IV. St. Lawrence River Basin. N. C. Grover, W. G. Hoyt, A. H. Horton, C. C. Covert and C. H. Pierce. Prepared in coöperation with the states of Wisconsin, New York, and Vermont. Water-Supply Paper 474. 110 pp. Paper, 15 cents.

BUREAU OF MINES

Monthly Statement of Coal-Mine Fatalities in the United States, June 1920. W. W. Adams. 13 pp. Paper, 5 cents.

BUREAU OF STANDARDS

Permeability of Rubber to Gases. J. D. Edwards and S. F. Pickering. Scientific Paper 287. 36 pp. Paper, 10 cents. 1920. The permeability of rubber compounds varies with the composition. The relative permeability of rubber to some common gases is shown in the following summary:

Gas	Relative Permeability (Hydrogen = 1)
Nitrogen	0.16
Air	0.22
Argon	0.26
Oxygen	0.45
Helium	0.65
Hydrogen	1.00
Carbon dioxide	2.9
Ammonia	8.0
Methyl chloride	18.5
Ethyl chloride	200.0

Recommended Specifications for Volatile Mineral Spirits for Thinning Paints. Prepared and recommended by the United States Interdepartmental Committee on Paint Specification Standardization, July 26, 1920. Circular 98. 6 pp. Issued August 24, 1920. These specifications apply only to petroleum distillates, known as mineral spirits. General specifications are outlined and directions are given for the detection and removal of separated water, sampling, laboratory examination, and basis of purchase.

The Two Common Failures of the Clark Standard Cell. E. C. McKelvy and M. P. Shoemaker. Scientific Paper 390. 12 pp. Paper, 5 cents.

Automatic Apparatus for Intermittent Testing. G. W. Vinal and L. M. Ritchie. Technologic Paper 171. 7 pp. Paper, 5 cents.

DEPARTMENT OF AGRICULTURE

The Process of Ripening in the Tomato, Considered Especially from the Commercial Standpoint. C. E. Sando. Department Bulletin 859. 38 pp. Paper, 10 cents. Issued September 7, 1920.

The Castor-Oil Industry. J. H. Shrader. Department Bulletin 867. 40 pp. Issued September 3, 1920.

Experiments on the Toxic Action of Certain Gases on Insects, Seeds, and Fungi. I. E. Neifert and G. L. Garrison. Department Bulletin 893. 16 pp. Paper, 5 cents. Issued September 8, 1920.

Proceedings of Conference of Men Engaged in Grain Dust Explosion and Fire Prevention Campaign Conducted by the United States Grain Corporation in Coöperation with the Bureau of Chemistry. 159 pp. Copies of this publication may be obtained upon application to the Bureau of Chemistry.

Articles from the Journal of Agricultural Research

Investigations in the Ripening and Storage of Bartlett Pears. J. R. Magness. 19 (August 16, 1920), 473–500.

COMMERCE REPORTS—SEPTEMBER, 1920

Germany plans to release 30,000 to 50,000 tons of **nitrogen,** which has been made by the Haber process from air, to be exported duty-free. The prices charged to German domestic fertilizer consumers will be reduced by the use of the receipts of sales made abroad. (P. 1062)

Bituminous limestones (asphalt) are being distilled in Palestine and Syria to meet the pressing demand for lubricating oil. (P. 1077)

The Italian production of **copper sulfate** in 1920 it is estimated will be ample to supply domestic needs. (P. 1099)

The outlook for the London **tin** market is said to be more optimistic than for some time past. (Pp. 1105–6)

The Alsatian **potash industry** is reviewed. The production for 1920 is estimated at 1,320,000 metric tons of crude salts; for 1921, 2,040,000 metric tons; and for 1922, 2,340,000 metric tons. Of the amount produced, about 33 per cent is utilized in France and 66 per cent is exported. (Pp. 1108–12)

The production of **santonin** in Russia is reviewed. (P. 1113)

Recent researches have shown that the amount of **lignite** existing in the subsoil of Italy in the deposits explored up to the present time may be estimated at about 270,000,000 tons. (P. 1114)

The Government will not exercise the option extended by the Reparation Commission upon impounded stocks of **chemical drugs** of German manufacturers or upon stocks of chemical drugs manufactured during the months January 1920 to June 1920, inclusive. It will, however, retain its right to participate in allotments from future daily production of chemical drugs which may be manufactured in Germany during the next four and one-half years. (P. 1126)

The United States Government has decided to exercise its option upon **German impounded dyestuffs,** and has authorized the Textile Alliance, Inc., to purchase these stocks in the interest of the American consumer. No dyes from these stocks may be imported which are either manufactured here, or for which suitable substitutes are manufactured here, on reasonable terms as to price, quality, and production. (Pp. 1134–5)

Attention is called to the importance of the **mineral resources** of the South Pacific Islands. Chrome, cobalt, and nickel are found in abundance; antimony, mercury, silver, lead, and copper have also been found. Nickel ore, nickel matte, and chrome ore constitute the chief exports. (P. 1139)

The cultivation of the **guinea oil palm** is being encouraged in the Philippine Islands. It produces two classes of oil, one from the fruit itself and one from the kernel. The cultivation of this palm is said to be more profitable than that of coconuts. (P. 1144)

It is estimated that approximately 44.4 per cent of the **paper** produced in the former Austro-Hungarian Empire in 1913 was manufactured in the present territory of Czechoslovakia. From April 15 to June 30, 1920, paper and pulp products held the first place among the Czecho-Slovak exports. (Pp. 1153–6)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by Japan during 1917, 1918, and 1919. (Pp. 1174–5)

Indications of **oil** are reported in Guppeland, Victoria, where the formation of the country is said to be similar to that of other oil-bearing centers. Bituminous shale, natural gas, mica, copper, and other valuable minerals are also believed to be present in this region. (P. 1180)

Important deposits of **barytes** are now being developed in South Australia. Certified analysis has shown this product to be of unsurpassed purity. (P. 1181)

According to a recent agreement, Belgium will receive for two years 240,000 tons of Australian **zinc ore**. (P. 1197)

Statistics are given showing the imports of **rubber** into Canada during the three years ended March 31, 1920. Since there is only one firm in British Columbia interested in the manufacture of rubber goods there is an excellent opportunity for American-made products. (Pp. 1208–12)

The **petroleum** industry of Mexico, which ranks second in oil production and has the greatest demonstrated supply, is reviewed in detail. From the following table it will be seen that the Mexican production of oil has multiplied more than three times in the last seven years. The production is reported in barrels of 42 gallons.

YEAR	Mexico Bbls.	United States Bbls.	World Bbls.
1913	25,902,439	248,446,230	384,667,550
1914	21,188,427	265,762,535	399,667,168
1915	32,910,508	281,104,104	426,370,894
1916	39,817,402	300,767,158	459,433,319
1917	55,292,770	335,315,303	505,362,367
1918	63,828,327	355,927,716	514,729,354
1919	87,359,533	377,719,000	......

(Pp. 1213–31)

The total production of **pig iron** in Canada during the first half of 1920 was 502,667 short tons, as compared with a production of 524,977 tons during the first half of 1919, and 392,804 tons during the second half of 1919. (P. 1241)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by Spain during 1917, 1918, and 1919. (P. 1251)

The **artificial silk** trade of the United States, which is rapidly developing an absolutely new domestic industry, is reviewed. (Pp. 1252–7)

The following table gives comparative statistics of the export of **rubber** from the Straits Settlements:

MONTH	1918 Tons	1919 Tons	1920 Tons
January	4,302	14,404	13,125
February	2,334	15,666	17,379
March	8,858	20,908	5,931
April	6,584	10,848	15,720
May	13,587	15,845	15,617
June	6,515	5,059	11,663
July	1,978	7,818	10,773
TOTAL	44,158	90,543	90,208

(P. 1290)

Statistics are given of the imports and exports of **vegetable oil** and vegetable-oil material by Switzerland during 1917, 1918, and 1919. (Pp. 1300–1)

The Chemical Works Department of Glasgow Corporation proposes to manufacture chemicals from **gas residuals**. The principal chemicals to be manufactured will be motor benzene, pure benzene, toluene, solvent and heavy naphthas, and carbonic acid. The advisability of making dyes and intermediates will also be considered. (P. 1312)

The French commission charged with the study of all matters relating to the production and utilization of **substitutes for coal** in its first annual report urges the French government to occupy itself with research work in France and its colonies and favor private initiative engaged in the work of prospecting and drilling for oil. The government is also urged to develop the production of peat and lignite, to take an inventory of the wood resources of France, and to encourage the utilization of certain classes of wood for fuel. (P. 1315)

The year 1919 was unfavorable for the Swedish **dye** industry. (P. 1316)

Of the total amount of **aniline dyes** imported into China during 1919, over 50 per cent came from the United States, about 25 per cent from Japan, the remainder being of French and other origin. Prior to the war German dyes practically monopolized the China market. Some of the dyes sell for such ridiculously low prices that it seems safe to assume that they are imitations. (Pp. 1322–3)

A new **camphor** producing center is reported at Burma. (P. 1324)

The available supply of **ferromanganese** in India is seriously affected because of the shortage of many thousands of wagons on the Indian railways and the congested condition of traffic. (Pp. 1324–5)

A good market for American **dyes** is reported in Western Greece. The colors most desired are black, navy blue, brown, green, red, and orange. (P. 1331)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by British India during the fiscal years ending March 31, 1918, 1919, and 1920. (P. 1336)

The stocks of the German firms which in pre-war times controlled the Serbian trade in **aniline dyes** have been taken over by a Serbian company with a practical monopoly of the trade for the time being. (P. 1339)

It is believed that the great number of **chromium ore** deposits in Russia and their nearness to metallurgical centers will give them much importance when conditions are again normal and proper methods of exploitation are adopted. The United States is the most important consuming country, using over 50 per cent of the world's production. (P. 1342)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by France during 1917, 1918, and 1919. (Pp. 1353–5)

Specifications of the special apparatus used in testing **Portland cement** in Chosen are given. (Pp. 1358–9)

A board of administration for the promotion of the German **textile industries** on a scientific basis has been created. The purposes of the board are the scientific investigation of domestic and foreign vegetable fibers, the question of substitutes, the search for and utilization of vegetable fibers grown in Germany which, up to the present time, have not been used, and the improvement in the production of artificial fibers and substitutes. (P. 1364)

At a recent meeting of the stockholders of the Potash Syndicate at Wintershall the stockholders demanded that, in order to be sure of regular export orders, **potash** prices should be reduced, especially for America. (P. 1364)

The **mineral** production in South Africa is reviewed, and a summary is given of the mineral production for May 1920. (P. 1366)

A heavy increase is reported in the price of **gasoline** in the United Kingdom. Gasoline substitutes are expected to play an important part in supplying fuel for motors until the potentially rich fields commence production and others become accessible. (P. 1373)

Possible developments in Russia's **chemical industry** and trade are noted. It is anticipated that the dye and wood distilling industries will do business on a larger scale. The operation of factories for the treatment of fats will be delayed by the shortage of fats. The most important item of the chemical industry in Russia is artificial fertilizers. A project is under way to obtain nitric acid from the air. (Pp. 1397–1401)

Specifications are given for **Portland cement** used by the Victorian Public Works Department and the Melbourne Board of Works. (P. 1402)

Statistics are given showing the imports and exports of **vegetable oil** and vegetable-oil material by the United Kingdom during 1917, 1918, and 1919. (Pp. 1413–5)

The **juice** of the **nipah palm** is said to contain 12 per cent of sugar. Experiments have shown that the process of extraction is commercially possible. In British North Borneo there are about 300,000 acres of nipah palm. In the Philippines, alcohol has been obtained from this palm for use as a beverage and as a fuel. (P. 1416)

Considerable deposits of **rock salt** have been discovered in New Greece. (P. 1457)

The **rubber** and rubber goods markets in Latin America are reviewed. (Pp. 1476–8)

Statistics are given on the imports and exports of **vegetable oil** and vegetable-oil material by the Dutch East Indies during 1917, 1918, and 1919. (Pp. 1491–2)

The **iron ore** resources of the world are reviewed. (Pp. 1498–1507)

SPECIAL SUPPLEMENTS ISSUED IN SEPTEMBER

FRANCE—7*b*
PORTUGAL—14*a*
LITHUANIA—16*a*
SPAIN—18*a*
SWITZERLAND—20*a*
BRITISH WEST INDIES—25*b*
DOMINICAN REPUBLIC—29*a*
DUTCH WEST INDIES—30*a*
STRAITS SETTLEMENTS—59*a*
BRITISH SOUTH AFRICA—69*a*
VIRGIN ISLANDS OF THE UNITED STATES—77*a*

STATISTICS OF EXPORTS TO THE UNITED STATES

LONDON—(Pp. 1350–1)
- Rubber
- Hides
- Drugs and chemicals
- Tin
- Leather
- Lead
- Creosote oil
- Nitrogenous fertilizer
- Copper
- Aluminium
- Dynamite glycerol
- Gums
- Linseed oil

CEYLON—(P. 1325)
- Rubber

MADAGASCAR—(P. 1179)
- Beeswax
- Graphite

GREAT BRITAIN (Pp. 1093–4)
- Salt (not table)
- Hides (undressed)
- Cement (calcareous)
- Iron
- Steel
- Lead manufactures
- Tin
- Ammonium sulfate
- Bleaching powder

CANADA—(P. 1469)
- Paper
- Chemical pulp
- Mechanical pulp

PORTUGAL—(P. 1071)
- Rubber

TRINIDAD—(P. 1338)
- Tonca beans

SHANGHAI (P. 1067)
- Antimony
- Albumin
- Camphor

ITALY—(P. 1488)
- Citrate of lime

PALERMO—(P. 1407)
- Citric acid
- Tartaric acid
- Sulfur oil

NETHERLANDS EAST INDIES—(P. 1375)
- Quinine
- Cinchona bark

PHILIPPINE ISLANDS—(P. 1144)
- Guinea oil

BOOK REVIEWS

Practical Standardization by Chemical Assay of Organic Drugs and Galenicals. By A. B. LYONS, F.C.S. 397 pp. Nelson, Baker & Co., Detroit, 1920. Price, $3.50.

No other book covers quite the same field as this, and for years there has been a dearth of properly compiled information such as it presents. Twenty-two years ago Dr. Lyons published a rather brief "Handbook of Chemical Assay of Drugs and Galenicals," which has served as the basis for this much more elaborate and comprehensive work. Dr. Lyons has been intimately in touch with the assay of drugs and medicinal substances for a great portion of his life, and is well fitted to speak with authority on the subject whereof he writes. The present volume goes much farther than the determination of alkaloidal or glucosidal constituents in drugs, and embraces also such subjects as the determination of solvents used in medicinal products; the valuation of some of the nonpotent vegetable drugs, for example, acacia, capsicum, licorice, mustard, etc.; a very brief statement of the essential characteristics of those volatile oils most frequently used in medicinal compounds, and methods for determination of the chief constituents of a few of the most important; approved methods of assay for some 40 or 50 organic medicinal substances, chiefly synthetic, for example, acetanilide, antipyrin, benzaldehyde, camphor, chloroform, ethyl nitrite, glycerophosphates, iodoform, lecithins, nitroglycerin, phenol, etc.; a brief chapter on the estimation of starch, cane sugar, lactose and glucose; one upon the assay of diastase, pancreatin, papain and pepsin, and some concise information on the chemical assay of suprarenal and thyroid glands.

Within so small a volume it would seem impossible to incorporate adequate information regarding the detailed testing of so large a number of substances, but the various assay methods are efficiently condensed and frequent journal references are given to the original source of information.

The book deserves a place in every laboratory having to do with the assay of medicinal substances, and, while primarily written for the experienced chemist, it will surely prove an excellent handbook in connection with teaching of drug analysis.

Chemists of experience in this particular line of work will not always agree with the author as to the preferred method of assay, but the entire field has been dealt with in a broad-minded way, and methods are given to suit varied conditions and different ideas.

The book itself is of convenient size, of good typographical makeup and contains comparatively few typographical errors. Each paragraph is introduced by black-faced type, indicating its contents, and is also numbered for convenience of indexing and cross reference. Last, but not least in a book of this kind, it possesses a good index. FRANK O. TAYLOR

Les Colloides Métalliques. Propriétés et Préparations. By PAUL BARY, Consulting Engineer, formerly Director of the School of Physics and Chemistry and of the Central Laboratory of Electricity. viii + 95 pp., 13 figures, 6 tables. Dunod, Paris, 1920. Price, 5 fr. 50.

The subject matter of this book is somewhat broader in scope than is indicated by the title; for, in addition to the metals such as Pt, Au, Ag, Cu, etc., C, P, S, Se, and Te are also dealt with in detail. The book is divided into four chapters. Chapter I, comprising 29 pages, is devoted to the discussion of the fundamental properties of suspensoids. In this limited space the treatise is necessarily elementary and incomplete. On the contrary, Chapters II and III, dealing with the methods of chemical and electrical colloidation, have been written with a very considerable effort toward comprehensive thoroughness. Chapter IV, on applications, contains a review of the many uses to which colloidal metals have been put. Their employment as catalytic agents is especially well dealt with, and the six pages of bibliography on this important phase of the subject will doubtless prove of great value to the chemist. The entire work is written in a pleasing scientific style devoid of flourish or circumlocution, and is well up to date.

ELLWOOD B. SPEAR

NEW PUBLICATIONS

Catalog: Chemical Engineering Catalog. 1450 pp. Price, $7.50, postpaid (Leasing privilege $2.00; in foreign countries, $3.50). The Chemical Catalog Co., Inc., New York.

Chemical Industry: L'Appareillage Mécanique des Industries Chimiques. A. Parnicke. French translation by E. Campagne. 356 pp. Illustrated. Price, 34 fr. Dunod, Paris.

Chemical Reactions, Their Theory and Mechanism. K. George Falk. 220 pp. Price, $2.50. D. Van Nostrand Co., New York.

Dyes: A Text-Book of Dye Chemistry. Georg von Georgievics and Eugène Grandmougin. Translated and revised from 4th German edition. 560 pp. Price, 30s. net. Scott, Greenwood & Son, London.

Fertilizers: Chemical Fertilizers and Parasiticides. S. Hoare Collins. 285 pp. Illustrated. (Industrial Chemical Series.) Price, $3.50. D. Van Nostrand Co., New York.

Handbook: Chimie. Émile Javet. 426 pp. Price, 8 fr. Dunod, Paris.

Handbook: Metallurgie. David Levat. 336 pp. Illustrated. Price, 8 fr. Dunod, Paris.

Hydraulic Tables. Gardner S. Williams and Allen Hazen. 3rd ed., revised. 115 pp. 6 × 9. Price, $2.00. John Wiley & Sons, Inc., New York.

Manual of Chemical Plant. S. S. Dyson. 2nd ed. Price, £2 5s. net. The Dover Printing and Publishing Co., Ltd., Dover, England.

Metallurgy: Lecons de Sidérurgie. Anglès d'Auriac. 714 pp. Illustrated. Price, 74 fr. Dunod, Paris.

Margarine. William Clayton. (Monographs on Industrial Chemistry.) 187 pp. Illustrated. Price, $4.75. Longmans, Green & Co., New York.

Mine Gases and Ventilation. James T. Beard. 2nd ed. 433 pp. Price, $4.00. McGraw-Hill Book Co., Inc., New York.

Minerals: Die Technisch Wichtigen Mineralstoffe: Übersicht ihres Vorkommens und ihrer Entstehung. K. Mieleitner. Illustrated. Price, M 19.40. R. Oldenbourg, München and Berlin.

Modern Electroplater. Kenneth M. Coggeshall. 276 pp. Illustrated. Price, $3.00. The Norman W. Henley Publishing Co., New York.

Resins: Gewinnung und Verarbeitung von Harz und Harzprodukten. G. Austerweil and J. Roth. Illustrated. Price, M 16.25. R. Oldenbourg, München and Berlin.

Theoretical Chemistry: Einfuhrung in die Mathematische Behandlung de Naturwissenschaften. W. Nernst and A. Schönflies. Illustrated Price, M 23.75. R. Oldenbourg, München and Berlin.

RECENT JOURNAL ARTICLES

Alcohol: L'Alcool, Nuovo Sottoprodotto della Distillazione del Carbon Fossile. Carlo Formenti. *Giornale di Chimica Industriale ed Applicata*, Vol. 2 (1920), No. 8, pp. 441–442.

Alloys: Heat Resisting Alloys for Case Carburizing. H. H. Harris. *The American Drop Forger*, Vol. 6 (1920), No. 9, pp. 446–448.

Arsenic: The Manufacture of White Arsenic. E. C. Williams. *Engineering and Mining Journal*, Vol. 110 (1920), No. 14, pp. 671–673.

Artificial Silk Industry in Japan. K. Yamada. *The Chemical Age* (London), Vol. 3 (1920), No. 65, p. 282.

Briquets: Good Briquets Made of Oklahoma Coal with Crude-Oil Residue as a Binder. J. C. Davis. *Coal Age*, Vol. 18 (1920), No. 9, pp. 443–444.

Camphor: The Distillation of Camphor in India. John Lionel Simonsen and Tarak Prosad Ghose. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 16, pp. 296*t*–298*t*.

Canadian Pulpwood Resources. D. M. Le Bourdais. *Paper*, Vol. 27 (1920), No. 4, pp. 19, 42, 44.

Catalysts: The Preparation of Catalysts. A. A. Pollitt. *The Chemical Age* (London), Vol. 3 (1920), No. 62, pp. 200–201.

Chemistry and Engineering: The Field for Co-operation between the Chemist and the Engineer. T. Linsey Crossley. *Canadian Chemical Journal*, Vol. 4 (1920), No. 9, pp. 243–246.

Coal-Saving in the Chemical Industry: The Scientific Control of Steam Boiler-Plant. David Brownlie. *The Chemical Trade Journal and Chemical Engineer*, Vol. 67 (1920), No. 1735, pp. 247–250; No. 1737, pp. 311–314; No. 1738, pp. 343–347.

Coal-Tar Chemicals: New Developments in Coal-Tar Chemicals and Specialties. Herbert G. Sidebottom. *Chemical Age*, Vol. 28 (1920), No. 9, pp. 311–312.

Combustion: Draft Combustion and Boiler Stacks. F. J. Denk. *Blast Furnace and Steel Plant*, Vol. 8 (1920), No. 10, pp. 575–577.

Copper: Diffusion of Solid Copper in Liquid Aluminium. Robert J. Anderson. *Chemical and Metallurgical Engineering*, Vol. 23 (1920), No. 12, pp. 575–577.

Corn-Cob Utilization: A Practical Study of Corn-Cob Utilization. Frederick B. La Forge. *Chemical Age*, Vol. 28 (1920), No. 9, pp. 332–336.

Distillation Plant, with Special Reference to the Rectification of Alcohol, Acetaldehyde, and Other Volatile Products, and Continuous Ether Manufacturing Plant. Stephane Masfaraud. *Journal of the Society of Chemical Industry*, Vol. 39 (1920), No. 17, pp. 299*t*–305*t*.

Dyes: Identification and Properties of Direct Cotton Yellow. Louis G. Hayes. *Color Trade Journal*, Vol. 7 (1920), No. 3, pp. 86–91.

Dyes: Standard Methods for Testing Dyestuffs. Walter M. Scott. *American Dyestuff Reporter*, Vol. 7 (1920), No. 15, pp. 14–16.

Dyes: The American Industry in Dyestuff Intermediates. D. H. Killeffer. *Textile World Journal*, Vol. 58 (1920), No. 13, pp. 52–53.

Dyes: The Use of the Tint Photometer in the Evaluation of Dyestuffs and Pigments. H. B. Gordon. *Textile Colorist*, Vol. 42 (1920), No. 502, pp. 699–703.

Foods: Chimie et Industrie de l'Alimentation: La Conservation des Viandes et les Abattoirs Industriels. Paul Razous. *L'Industrie Chimique*, Vol. 7 (1920), No. 80, pp. 298–301.

Fuels: Recent Patents on Mixed Fuels. W. R. Ormandy. *Journal of the Institution of Petroleum Technologists*, Vol. 6 (1920), No. 23, pp. 229–239.

Gas Fuel: Advantages of Gas Fuel in the Heat Treatment of Metals. R. G. Logue. *American Gas Engineering Journal*, Vol. 113 (1920), No. 15, pp. 283–286.

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Hydrosulfites: Report of the Estimation of Hydrosulfites and Sulfoxylates. Edward L. Helwig. *American Dyestuffs Reporter*, Vol. 7 (1920), No. 15, pp. 12–13.

Liquid Air: Rectification de l'Air Liquide. E. Barbet. *Chimie et Industrie*, Vol. 4 (1920), No. 2, pp. 147–150.

Metals: Briquetting of Metal Scrap. Adolph Bregman. *The Metal Industry*, Vol. 18 (1920), No. 9, pp. 400–402.

Motor Gasoline: Production of Motor Gasoline from Heavy Oil Hydrocarbons. Fred W. Padgett. *Chemical and Metallurgical Engineering*, Vol. 23 (1920), No. 11, pp. 521–525.

Motor Spirit: Possible Sources of Home-Produced Motor Spirit. E. de Barry Barnett. *The Chemical Age* (London), Vol. 3 (1920), No. 64, pp. 254–255.

Oil Shale Industry in Scotland and England. Victor C. Alderson. *American Gas Engineering Journal*, Vol. 113 (1920), No. 14, pp. 255–260, 265.

Optical Glass: The Manufacture and Uses of Rolled Optical Glass. H. S. Roberts and J. C. Hostetter. *Journal of the American Ceramic Society*, Vol. 3 (1920), No. 9, pp. 750–761.

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Overflow Volumeter: A Direct Reading Overflow Volumeter. H. G. Schurecht. *Journal of the American Ceramic Society*, Vol. 3 (1920), No. 9, pp. 730–734.

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Plating Solutions: Analysis of Plating Solutions. Joseph Haas, Jr. *The Metal Industry*, Vol. 18 (1920), No. 9, pp. 412–414.

Rubber: Some Aspects of the Stress-Strain Curve. William B. Wiegand. *India Rubber World*, Vol. 63 (1920), No. 1, pp. 18–21.

Smelting with Bituminous Coal in Blast-Furnaces. H. C. Robson. *Mining and Scientific Press*, Vol. 121 (1920), No. 12, pp. 409–412.

Steel: Surface Changes of Steels Heated in Vacuo. E. Heaton Hemingway and Geo. R. Ensminger. *The American Drop Forger*, Vol. 6 (1920), No. 9, pp. 436–441.

Textile Industry: Water and Its Application in the Textile Industry. Walter E. Hadley. *American Dyestuff Reporter*, Vol. 7 (1920), No. 15, pp. 10–12.

Ventilation: Improvements of Working Conditions by Mechanical Ventilation with Special Reference to Dyeworks and Chemical Works. J. E Brierley. *Journal of the Society of Dyers and Colourists*, Vol. 36 (1920), No. 9, pp. 233–237.

Welding Various Metals by Gas Methods. J. F. Springer. *Textile World Journal*, Vol. 58 (1920), No. 15, pp. 101–103.

MARKET REPORT—OCTOBER, 1920

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Oct. 1	Oct. 15
Acid, Boric, cryst., bbls.	lb.	.17	.17
Hydrochloric, com'l, 22°	lb.	.02¼	.02
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.07¾	.07¾
Phosphoric, 50% tech.	lb.	.25	.25
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	21.00	21.00
Oleum 20%	ton	25.00	23.00
Alum, ammonia, lump	lb.	.04¾	.04¾
Aluminium Sulfate (iron-free)	lb.	.04½	.04½
Ammonium Carbonate, pwd.	lb.	.16	.16
Ammonium Chloride, gran.	lb.	.14	.12½
Ammonia Water, carboys, 26°	lb.	.11	.11
Arsenic, white	lb.	.14	.14
Barium Chloride	ton	120.00	120.00
Nitrate	lb.	.14	.14
Barytes, white	ton	30.00	30.00
Bleaching Powd., 35%, Works,	100 lbs.	6.75	6.75
Borax, cryst., bbls.	lb.	.09½	.09½
Bromine, tech.	lb.	.55	.55
Calcium Chloride, fused	ton	33.50	33.50
Chalk, precipitated, light	lb.	.05	.05
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	7.50	7.50
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	4.35	4.35
Lead Acetate, white crystals	lb.	.13	.13
Nitrate	lb.	.15	.15
Red American	100 lbs.	.12¼	.12¼
White American	100 lbs.	.10½	.10½
Lime Acetate	100 lbs.	3.50	3.50
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, Tech.	lb.	.13	.13
Magnesite	ton	65.00	65.00
Mercury flask	75 lbs.	70.00	65.00
Phosphorus, yellow	lb.	.35	.35
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.32	.31
Bromide, Cryst.	lb.	.50	.45
Carbonate, calc., 80–85%	lb.	.20	.20
Chlorate, cryst.	lb.	.18	.18
Hydroxide, 88–92%	lb.	.22	.22
Iodide, bulk	lb.	3.25	3.25
Nitrate	lb.	.14	.12
Permanganate, U. S. P.	lb.	.70	.65
Salt Cake	ton	Nominal	Nominal
Silver Nitrate	oz.	.59	.55
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.65	2.50
Caustic, 76%	100 lbs.	4.00	4.25
Sodium Acetate	lb.	.12	.12
Bicarbonate	100 lbs.	3.00	3.00
Bichromate	lb.	.17	.10½
Chlorate	lb.	.10	.10
Cyanide	lb.	.30	.30
Fluoride, technical	lb.	.20	.20
Hyposulfite, bbls.	100 lbs.	4.00	4.00
Nitrate, 95%	100 lbs.	3.50	3.00
Silicate, 40°	lb.	.01½	.01½
Sulfide	lb.	.08½	.08½
Bisulfite, powdered	lb.	.07	.07
Strontium Nitrate	lb.	.15	.15
Sulfur, flowers	100 lbs.	3.75	4.00
Crude	long ton	25.00	25.00
Talc, American, white	ton	20.00	20.00
Tin Bichloride	lb.	.21½	.21½
Oxide	lb.	.60	.60
Zinc Chloride, U. S. P.	lb.	.50	.50
Oxide, bbls.	lb.	.12	.12

ORGANIC CHEMICALS

		Oct. 1	Oct. 15
Acetanilide	lb.	.50	.45
Acid, Acetic, 28 p. c.	100 lbs.	3.75	3.75
Glacial	lb.	.12	.12
Acetylsalicylic	lb.	.85	.85
Benzoic, U. S. P., ex-toluene	lb.	.80	.80
Carbolic, cryst., U. S. P., drs.	lb.	.15	.15
50- to 110-lb. tins	lb.	.23	.23
Citric, crystals, bbls.	lb.	.70	.65
Acid (*Concluded*)			
Oxalic, cryst., bbls.	lb.	.38	.32
Pyrogallic, resublimed	lb.	2.35	2.35
Salicylic, bulk, U. S. P.	lb.	.45	.40
Tartaric, crystals, U. S. P.	lb.	.65	.61
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.22	.22
Alcohol, denatured, 190 proof	gal.	1.13	1.13
Ethyl, 190 proof	gal.	6.00	5.50
Wood, Pure	gal.	3.75	3.40
Amyl Acetate	gal.	4.00	4.00
Camphor, Jap. refined	lb.	1.20	1.20
Carbon Bisulfide	lb.	.08	.08
Tetrachloride	lb.	.14½	.12
Chloroform, U. S. P.	lb.	.43	.43
Creosote, U. S. P.	lb.	.70	.70
Cresol, U. S. P.	lb.	.18	.18
Dextrin, corn	lb.	.06¼	.06¼
Imported Potato	lb.	.11	.11
Ether, U. S. P., conc., 100 lbs.	lb.	.24	.24
Formaldehyde	lb.	.40	.27
Glycerol, dynamite, drums	lb.	.27	.25
Pyridine	gal.	2.75	2.75
Starch, corn	100 lbs.	4.23	4.23
Potato, Jap.	lb.	.06½	.06½
Rice	lb.	.25	.25
Sago	lb.	.05	.05

OILS, WAXES, ETC.

		Oct. 1	Oct. 15
Beeswax, pure, white	lb.	.60	.60
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.14½	.14½
Ceresin, yellow	lb.	.13	.13
Corn Oil, crude	lb.	.08½	.08½
Cottonseed Oil, crude, f. o. b. mill	lb.	.09½	.07¾
Menhaden Oil, crude (southern)	gal.	.50	.50
Neat's-foot Oil, 20°	gal.	1.65	1.65
Paraffin, 128–130 m. p., ref.	lb.	.11½	.11½
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	13.00	12.90
Rosin Oil, first run	gal.	.72	.72
Shellac, T. N.	lb.	.95	.90
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.85	1.85
Stearic Acid, double-pressed	lb.	.19½	.19½
Tallow Oil, acidless	gal.	1.25	1.25
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	1.38	1.27

METALS

		Oct. 1	Oct. 15
Aluminium, No. 1, ingots	lb.	.32	.28
Antimony, ordinary	100 lbs.	7.25	6.75
Bismuth	lb.	2.72	2.72
Copper, electrolytic	lb.	.18¾	.16
Lake	lb.	.18¾	.16½
Lead, N. Y.	lb.	.07¾	.07¼
Nickel, electrolytic	lb.	.45	.45
Platinum, refined, soft	oz.	110.00	110.00
Quicksilver, flask	75 lbs ea.	70.00	65.00
Silver	oz.	1.00	1.00
Tin	lb.	.43	.37½
Tungsten Wolframite	per unit	6.50	6.50
Zinc, N. Y.	100 lbs.	7.60	7.35

FERTILIZER MATERIALS

		Oct. 1	Oct. 15
Ammonium Sulfate	100 lbs.	5.35	4.80
Blood, dried, f. o. b. N. Y.	unit	8.00	8.00
Bone, 3 and 50, ground, raw	ton	48.00	48.00
Calcium Cyanamide, unit of Ammonia		4.00	4.00
Fish Scrap, domestic, dried, f. o. b. works	unit	7.25	7.25
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	6.85	6.85
Tennessee, 78–80%	ton	11.00	11.00
Potassium Muriate, 80%	unit	2.25	1.75
Pyrites, furnace size, imported	unit	.18	.18
Tankage, high-grade, f. o. b. Chicago	unit	7.75	7.75

COAL-TAR CHEMICALS

Crudes

		Oct. 1	Oct. 15
Anthracene, 80–85%	lb.	.75	75
Benzene, Pure	gal.	.35	.35
Cresol, U. S. P.	lb.	.18	.18
Cresylic, 97–99%	gal.	1.20	1.20
Naphthalene, flake	lb.	.13 1/2	.10 1/2
Phenol, drums	lb	.15	.15
Toluene, Pure	gal.	.35	.35
Xylene, 2 deg. dist. range	gal.	.60	.60

Intermediates

		Oct. 1	Oct. 15
Acids:			
Anthranilic	lb.	2.20	2.20
B	lb.	2.25	2.25
Benzoic	lb.	.80	.80
Broenner's	lb.	1.75	1.75
Cleve's	lb.	2.00	2.00
Gamma	lb.	4.25	4 00
H	lb.	1.80	1.70
Metanilic	lb.	1.70	1.70
Monosulfonic F	lb.	3.50	3.50
Napthionic, crude	lb.	.85	85
Nevile & Winther's	lb.	1.90	1.80
Phthalic	lb.	.60	.60
Picric	lb.	.25	.25
Sulfanilic	lb.	.33	.33
Tobias	lb.	2.25	2.25
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.27 1/2	.26
For Red	lb.	.65	.65
Aniline Salt	lb.	.33	.33
Anthraquinone	lb.	3.00	2.50
Benzaldehyde, tech	lb.	.65	.65
U. S. P.	lb.	1.00	1.00
Benzidine (Base)	lb.	1.25	1.15
Benzidine Sulfate	lb.	1.05	1.05
Diaminophenol	lb.	6.00	5.50
Dianisidine	lb.	9.00	8.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.55	1.50
Dimethylaniline	lb.	.90	.90
Dinitrobenzene	lb.	.36	.36
Dinitrotoluene	lb.	.43	.43
Diphenylamine	lb.	.80	.80
G Salt	lb.	.85	.80
Hydroquinone	lb.	2.20	2.00
Metol (Rhodol)	lb.	6.75	6.75
Monochlorobenzene	lb.	.15	.14
Monoethylaniline	lb.	2.15	2.15
a-Naphthylamine	lb.	.45	.45
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist.	lb.	.68	.50
m-Nitroaniline	lb.	1.05	.90
p-Nitroaniline	lb.	1.25	1.15
Nitrobenzene, crude	lb.	.14	.14
Rectified (Oil Mirbane)	lb.	.16	.16
p-Nitrophenol	lb.	.80	.80
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.25	.25
p-Nitrotoluene	lb.	1.50	1.50
m-Phenylenediamine	lb.	1.45	1.30
p-Phenylenediamine	lb.	2.30	2.30
Phthalic Anhydride	lb.	.65	.65
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.90	.85
Resorcinol, tech	lb.	2.25	2.25
U. S. P.	lb.	2.75	2.75
Schaeffer Salt	lb.	.75	.75
Sodium Naphthionate	lb.	1.10	1.10
Thiocarbanilide	lb.	.60	.60
Tolidine (Base)	lb.	1.75	1.75
Toluidine, mixed	lb.	.44	.44
o-Toluidine	lb.	.33	.33
m-Toluylenediamine	lb.	1.50	1.50
p-Toluidine	lb.	1.75	1.75
Xylidine, crude	lb.	.50	.50

COAL-TAR COLORS

Acid Colors

		Oct. 1	Oct. 15
Black	lb.	1.25	1.25
Blue	lb.	3.00	3.00

Acid Colors (*Concluded*)

		Oct. 1	Oct. 15
Fuchsin	lb.	2.50	2.50
Orange III	lb.	1.00	1.00
Red	lb.	1.30	1.30
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	5.50	5.50
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	12.00	12.00
Indigotin, conc.	lb.	3.00	3.00
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.95	1.95
Ponceau	lb.	1.25	1.25
Scarlet 2R	lb.	1.00	1.00

Direct Colors

		Oct. 1	Oct. 15
Black	lb.	1.00	1.00
Blue 2B	lb.	.70	.70
Brown R	lb.	1.65	1.65
Fast Red	lb.	3.50	3.50
Yellow	lb.	2.00	2.00
Violet, conc.	lb.	2.20	2.20
Chrysophenine, domestic	lb.	2.25	2.25
Imported	lb.	3.80	3.80
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Oct. 1	Oct. 15
Black	lb.	.70	.70
Blue	lb.	1.65	1.65
Orange	lb.	1.40	1.40
Red III	lb.	1.65	1.65
Scarlet	lb.	1.75	1.75
Yellow	lb.	1.70	1.70
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		Oct. 1	Oct. 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

		Oct. 1	Oct. 15
Alizarin Blue, bright	lb.	7.75	7.75
Alizarin Red, 20% Paste	lb.	1.10	1.10
Alizarin Yellow G	lb.	1.00	1.00
Chrome Black, domestic	lb.	1.25	1.25
Imported	lb.	2.20	2.20
Chrome Blue	lb.	2.50	2.50
Chrome Green, domestic	lb.	2.00	2.00
Chrome Red	lb.	2.00	2.00
Gallocyanin	lb.	3.25	3.25

Basic Colors

		Oct. 1	Oct. 15
Auramine, O, domestic	lb.	2.50	2.50
Auramine, OO	lb.	4.15	4.15
Bismarck Brown Y	lb.	.90	.90
Bismarck Brown R	lb.	1.20	1.20
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	6.00	6.00
Indigo, 20 p. c. paste	lb.	.85	.85
Fuchsin Crystals, domestic	lb.	6.50	6.50
Imported	lb.	12.00	12.00
Magenta Acid, domestic	lb.	4.25	4.25
Malachite Green, crystals	lb.	4.50	4.50
Methylene Blue, tech	lb	2.75	2.75
Methyl Violet 3 B	lb.	3.00	3.50
Nigrosine, spts. sol.	lb.	.85	.85
Water sol., blue	lb.	.70	.70
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc.	lb.	40.00	40.00
Victoria Blue, base, domestic	lb.	6.00	6.00
Victoria Green	lb	6.00	6.00
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00