1915

Sulfur, Pyrite and Sulfuric Acid

Samuel Henry Salisbury Jr.

SULPHUR, PYRITE AND SULPHURIC ACID

By Samuel H. Salisbury, Jr.

Sulphur

Last year the United States surpassed the other great sulphur-producing center—Sicily—and now occupies the dominating position in the sulphur industry of the world, Italy ranking second. This was due more to the decreased production by the Sicilian mines than to any large increase in production in the United States, which remained about normal.

The imports of crude sulphur into the United States during 1915 were 24,647 long tons valued at approximately $405,990, an increase over 1914 of almost 2000 long tons, the figures for the year 1914 being 22,810 long tons valued at $409,537. A considerable amount of this increase was due to the increased activity of the Japanese sulphur business, practically no Sicilian sulphur reaching this country last year.

Sulphur production in the United States in 1915 was probably the greatest in the history of the industry. Louisiana and Texas furnished practically the whole output, the former State supplying the major part of this production as heretofore. The Union Sulphur Co., at Sulphur, La., maintained in 1915 its normal yearly output of about 375,000 tons, with four wells. In Texas, the Freeport Sulphur Co. added a third steaming plant at the Bryan Heights dome and was producing at the end of 1915 at the rate of about 300 tons per day; no figures of the year's output were obtainable from the company. No production except for local consumption was made in other States of this country, and the same was true of the other Americas.

The sulphur trade in the United States was decidedly slack during the first half of 1915, but improved gradually until at the end of the year there was a brisk trade. Stocks at the end of 1915, however, were greater than at any previous time. The slack conditions in the paper trade in the first half of the year reduced domestic consumption in 1915 to less than 300,000 tons. Export business was practically suspended owing to transport conditions, but late in the year the Union Sulphur Co. made two small shipments to Sweden and purchased a 9000-ton steamer preparatory to resuming shipments to some of its European distributing stations. Prices remained practically stationary in the United States, but the Consorzio, which controls the Silician sulphur sales, is reported to have raised

its prices late in the year. Japan at midyear was producing at an increased rate.[1]

SULPHUR IMPORTS AND EXPORTS OF THE UNITED STATES
(In tons of 2240 lb.)

Kind.	1910.		1911.		1912.		1913.		1914.		1915.	
	Amt.	Value.	Amt.	Value.	Amt.	Value.	Amt.	Value.	Amt.	Value.	Amt.	Value
Imports:												
Crude.....	28,647	$495,988	24,250	$436,725	26,885	$494,778	14,636	$278,056	22,810	$409,537	24,647	$405,990
Flowers.....	912	30,180	3,891	83,491	1,310	39,129	5,899	115,574	621	17,214	647	23,146
Refined.....	985	25,869	986	24,906	1,665	40,933	1,234	29,091	1,800	47,568	988	30,335
Precipitated..	47	6,489	68	8,643	66	9,137	350	17,690	105	14,161	85	12,987
Total imports....	30,544	$552,037	29,127	$545,122	29,860	$574,837	22,119	$440,411	25,336	$488,490	26,367	$472,458
Exports.....	30,742	552,941	28,103	545,420	57,736	1076,414	89,221	1,559,761	98,163	1,807,334	37,312	724,679

MARKETED PRODUCTION OF SULPHUR IN THE UNITED STATES, 1880–1914, IN LONG TONS
(U. S. Geol. Surv.)

Year.	Quantity.	Value.	Year.	Quantity.	Value.
1904.....	127,292	$2,663,760	1910.....	255,534	$4,605,112
1905.....	181,677	3,706,560	1911.....	265,664	4,787,049
1906.....	294,153	5,096,678	1912.....	303,472	5,256,422
1907.....	293,106	5,142,850	1913.....	311,590	5,479,849
1908.....	369,444	6,668,215	1914.....	327,634	5,954,236
1909.....	239,312	4,432,066			

Sulphur Mining in the United States

Louisiana.—The Union Sulphur Co., at Sulphur, La., maintained in 1915 its normal yearly output of about 375,000 tons, with four wells.

Texas.—The opening of a sulphur mine at Freeport, Tex., near the mouth of the Brazos River, has given a new impetus to the sulphur industry in the United States and the splendid production that is being secured assures for this country another great source of supply of sulphur.

It has been known for years that there were deposits of sulphur at this point, but it was not until about 3 years ago that actual work in their successful operation began. Real operation began some 2 years ago and the success of the production up to this time leads to the conclusion that the Freeport sulphur mines will compare favorably with any in the world.

The sulphur produced at these mines is remarkably pure. While it is classed as crude, it is sold on a commercial guarantee of 99.5 per cent. pure, and it often grades as high as 99.9 per cent. pure.

The plant has been increased since the operation began, very materially. It now has a boiler capacity of 12,000 hp., and their energy is all

[1] *Eng. Min. Jour.*, Jan. 8, 1916.

devoted to the operation of the plant, which is in operation day and night. It has every modern appliance and is regarded as one of the most complete plants in the country.

An interesting experiment is now being undertaken in the hope of effecting a large economy in heating mine water. The natural heat of the subterranean water in the formation is 105°. As the water is now delivered to the plant for heating, its temperature varies with the season from 40 to 90°. To raise this water to a temperature of 336° obviously consumes more fuel than from 105°. The formation water, however, carries heavy scale-forming properties, and especial equipment has been designed to prevent the precipitation of this scale within the heaters or piping.

An area of several hundred acres, chiefly under the mound known as Bryan Heights, has been demonstrated as containing sulphur, and a complete plan of carrying on investigations as to the area is under way, so that the richest spots may be located. The present output is satisfactory, but there may be territory of much greater richness than now under devleopment, which will be determined by systematic exploration.

The plant is admirably located, in that it is within 3 miles of the port of Freeport, which has been improved to a depth of 18 ft.

Foreign Sulphur Industry

Chile.—(By Benjamin L. Miller and Joseph T. Singewald, Jr.). During 1915 the sulphur industry of Chile exhibited unusual activity and the production was much in excess of any previous year. Plans for still further increasing the output were formulated, and if carried out, will require the companies to look about for new markets for their product. At present the vineyards of south-central Chile consume practically the entire production.

Chile, and also Peru, contains a number of undeveloped sulphur deposits which, as yet, have received little attention. The sulphur is of volcanic origin and is found high up on the flanks of the recent extinct volcanoes that are such prominent features in the western range of the Andes. Many of these mountains still have active fumaroles and the sulphur is continually being formed from the sulphurous gases in the interstices of the rocks.

The greatest obstacle in the working of the deposits is due to the elevations at which they occur. Few of them are less than 14,000 feet above sea-level and some of the best are about 20,000 feet. The difficulties of working these highest deposits are so great that no efforts have been made to operate them. So far as known the highest deposist now worked are on the top of Mt. Olca at an elevation of 18,500 feet and on Mt. Chupiquina at about 19,000 feet.

The difficulties of transportation have hindered the development of the sulphur industry of the country and now, with two railroads crossing the belt, this has been in part remedied, but the greater number of deposits still remain untouched.

The active regions are two in number, the Ollague district along the line of the Antofogasta-La Paz Railroad and the Tacora district through which the Arica-La Paz railroad passes.

The Ollague workings are on the steep south slopes of Mt. Ollague a short distance below the great active fumarole that is continually emitting sulphurous gases and steam visible twenty miles away. There is a large quantity of practically pure sulphur, which alone is taken, while the rich sulphur rock or caliche, is discarded. The sulphur is taken to the railroad station at Ollague on the backs of llamas or burros.

On Mt. Olca which lies about 8 miles east of Yuma, a station on the Collahuasi branch railroad, and through the summit of which the Chilean-Bolivian boundary line passes, there are two companies engaged in mining sulphur. Here also only the pieces of practically pure sulphur are sacked for hauling to the railroad.

In the Tacora district four companies were in operation during 1915. Here the caliche is of lower grade and all of it is refined by volatilization before shipment. One company, Muecke and Co., have an aerial tram from their deposits high up on Mt. Chupiquina to Chislluma, about 5 kilometers away, where their oficina and refining retorts are located. Another company, Espada Hermanos, was engaged during the year in the construction of a narrow gauge steam railroad 22 kilometers in length to haul the caliche from the mines on Mt. Tacora to their oficina located along the Arica-La Paz railway between Ancora and Humapalca.

The Tacora district contains an abundance of yareta, a moss-like plant that forms thick compact masses on the rocks and contains much resinous material which makes it an excellent fuel. Without this useful plant growth the sulphur could not be refined in the district with profit

Japan.—The export of sulphur from Japan has for years been on the decline, and quotations have fallen, some of the sulphur mines of small standing having even been compelled to stop working. But since the war broke out the demand in the foreign market has improved, and quotations have gradually risen. The export to the end of August, 1915, was 27,948,607 lb., valued at $203,048, showing an increase of 4,638,451 lb. or $20,003, compared with the figures for the corresponding period of last year. The destinations have in the past been the United States and Australia in the main, with Canada and India coming next, only quite an insignificant amount being shipped to Europe. Since the war, how-

ever, the European supply to oriental countries has been stopped, and the demand in Europe itself has increased. Therefore, Japanese sulphur has now to meet an increased demand in the Orient and America and also in Europe. The prospects of this trade are, therefore, very promising, and it is expected that the volume of trade will soon become as big as it was several years ago when the sulphur trade was on the high tide of prosperity.[1]

Several orders for sulphur have been received by Japanese merchants from the United States and Australia. Already something like 10,000 tons, at $14.94 per ton, have been sold. Russia has begun to buy in Japan recently, though in small quantities. The visible stock in Osaka and Kobé has fallen off from 2000 tons to 1000 tons. In the producing districts also the stock is very small, and there is little prospect of its being replenished at an early date, as the mines will be closed for the winter months. The price is, in these circumstances, on the upgrade, the progress being quite rapid. Powder sulphur, especially, has increased rapidly in price. During November it advanced from $28 to $39.84 per ton.[2]

Italy.—Owing to the fact that the domestic supply of crude sulphur in the United States meets the demand, none was exported from Sicily to that country. Further, the United States now actively competes with Sicily in crude sulphur in the European markets. The decline in Sicilian exports is in part due to this competition, to the increased use of pyrites as a sulphur substitute, and to the paralysis of trade consequent to the war.

The production during the year was 334,974 metric tons, an amount less than the preceding year. In fact, the production for several years past has declined, probably due to lack of capital for financing and to the shutting down of some of the large mines on account of fires.

The increased cost of the extraction of the ore at the mines induced the producers to petition the government syndicate that controls the sale of the sulphur (Consorzio Obbligatorio per l'Industria Solfifera Siciliana) to advance prices, which request was granted in July, 1914.

The Consorzio's prices per metric ton of crude sulphur in bulk on board lighters at the port of Girgenti, Sicily, before and after July, 1914, are given in the following table:

Quality.	Purity.	Jan.–July.	Aug.–Dec.	Quality.	Purity.	Jan.–July.	Aug.–Dec.
	Per Cent.	Per Ton.	Per Ton.		Per Cent.	Per Ton.	Per Ton.
Yellow superior....	99	$19.30	$19.78	Brown superior.	96	$18.72	$19.20
Yellow inferior.....	97	19.11	19.59	Brown inferior.	95	18.53	19.01

[1] *Comm. Rept.*, Nov. 3, 1915.
[2] *Comm. Rept.*, Feb. 7, 1916.

Crude sulphur in bulk is seldom shipped from Catania. The Consorzio convey it here for refining and milling purposes and supply only enough to about fill the demand, and in order to discourage its export in the natural state from this port the syndicate has established a higher price from Catania than from Girgenti.

Refined and milled sulphurs which are chiefly exported from Catania met a fairly active demand during the year. Local competition is keen and profits small. Owing to the increased cost of refining, increased prices of bagging, and cost of wood for the casks, prices for sulphurs have advanced.

The market prices of refined and milled sulphur at the end of 1914, per metric ton f.o.b. Catania (in 112-lb. sacks), were as follows: Sublimed flower of sulphur, $34.35; refined sulphur in rolls, $27.98; refined sulphur in lumps, $28.79; and refined ground sulphur, $25.09.[1]

TOTAL EXPORTS OF SULPHUR FROM SICILY, 1906–1914
(In metric tons)

Country.	1907.(d)	1908.(d)	1909.(d)	1910.(d)	1911.(d)	1912.(d)	1913.(d)	1914.(d)	1915.(d)
Austria	26,390	22,086	26,560	29,601	34,136	38,362	36,335	25,306	70
Belgium	8,066	8,746	16,377	14,305	11,771	10,723	13,321	5,975	.....
France	59,868	96,448	90,239	93,229	114,868	104,109	21,582	60,773	96,156
Germany	35,059	30,229	28,538	30,225	28,664	32,286	31,042	18,826	391
Greece and Turkey	27,969	24,838	16,309	21,435	24,933	15,436	20,112	20,746	19,857
Holland	14,951	9,812	8,708	9,731	10,549	14,019	8,976	8,080	1,163
Italy	57,743	60,134	49,692	61,269	72,959	84,952	85,740	97,170	116,601
Portugal	13,328	17,586	21,036	18,758	25,121	21,314	21,445	17,604	21,004
Spain									
Scandinavia (c)	23,415	30,366	19,905	20,354	29,741	35,111	28,108	25,294	24,832
Russia	21,244	14,068	18,584	25,866	23,485	25,563	25,891	21,290	2,791
United Kingdom	17,929	20,597	19,860	19,074	19,936	19,830	16,052	12,991	36,156
United States	4,047	9,654	14,706	12,205	8,482	2,856	1,028	1,406	2,054
Other countries(b)	31,942	30,509	33,999	36,935	49,181	42,731	54,185	22,883	38,731
Totals	341,951	375,037	364,513	393,987	453,826	447,292	414,717	338,344	359,806
Stock in Sicily, Dec. 31	594,459	616,419	647,880	640,711	551,442	450,917	376,365	369,001	323,391

(a) Reported by Emil Fog & Sons, Messina. (b) Mainly South Africa, Northern Africa, Asia, Australia, and the East Indies. (c) Including Norway, Sweden and Denmark. (d) Reported by Parsons & Petit, New York. (e) Includes Canada.

New Zealand.—Sulphur deposits are found on White Island, in the Bay of Plenty on the coast of the North Island of New Zealand, about 30 miles from the main land. This island, which covers about 600 acres, attains a height of 900 ft. on one side and opens to the sea on the other. Its topography indicates an old crater, and the boiling lake on the island, which is one of the awe-inspiring sights of New Zealand, is a further evidence of volcanism. After the New Zealand Sulphur Co. had spent $100,000 in preparation for mining sulphur in this locality, a volcanic disturbance wrecked the camp and killed 10 men.[2]

[1] *Comm. Rept. Suppl.*, Aug. 18, 1915.
[2] *Min. Amer.*, Dec. 25, 1915.

WORLD'S PRODUCTION OF SULPHUR (a)
(In metric tons)

Year.	Austria. (b) (e)	Chile.	France. (b)	Germany.	Greece.	Italy. (b)	Japan.	Spain.	United States.	Total.
1898.....	589	1,256	9,818	1,954	135	502,351	10,339	(b)3,100	2,770	532,312
1899.....	671	989	11,744	1,663	1,150	563,697	10,241	1,100	1,590	592,290
1900.....	985	2,472	11,551	1,445	891	544,119	14,439	750	4,630	581,282
1901.....	5,048	2,516	6,836	963	2,336	563,096	16,548	610	6,977	604,930
1902.....	3,826	2,636	8,021	487	1,391	510,333	18,287	450	7,565	552,996
1903.....	4,610	3,560	7,375	219	1,266	553,751	22,914	1,680	35,660	631,035
1904.....	6,431	3,594	5,447	209	1,225	527,563	25,587	605	196,588	767,249
1905.....	8,542	3,470	4,637	205	1,126	568,927	24,652	610	218,440	830,609
1906.....	15,258	4,598	2,713	178	(d)1,000	499,814	27,589	700	298,704	845,956
1907.....	24,199	2,905	2,000	176	(d)1,000	426,972	33,329	3,612	312,731	801,911
1908.....	17,429	2,705	2,189	811	(d)1,000	445,312	33,419	13,872	312,700	829,437
1909.....	12,856	4,508	2,900	1,185	(d)1,000	435,060	36,317	21,750	303,000	817,608
1910.....	15,976	3,823	2,641	1,272	.....	430,360	43,848	30,113	259,699	787,732
1911.....	15,856	4,451	1,200	1,251	174	414,671	52,064	40,662	246,300	776,629
1912.....	14,979	4,431	1,000	(c)	2,016	357,547	55,005	42,344	308,530	785,852
1913	10,561	(c)	659	.....	*Nil*	349,602	59,481	62,653	316,783	.....
1914.....	.....	.....	.....	.....	*Nil*	403,558	.....	.....	333,095	.....

(a) From the official reports of the respective governments. The sulphur recovered as a by-product by the Chance-Claus process in the United Kingdom, amounting to between 20,000 and 30,000 long tons annually, is not included. (b) Crude mineral; limestone impregnated with sulphur. (c) Not yet reported. (d) Estimated. (e) Includes such production from Hungary.

PYRITE

Under normal conditions the United States imports about three times as much pyrite as it produces. During 1915, however, the amount imported was considerably less than usual due to high rates and scarcity of bottoms. The average prices were somewhat higher than heretofore, being about 15 cts. per unit as against 13½ before the war. It is estimated that the amount of pyrite imported from Spanish and Portuguese ports during 1915 was not much over 900,000 tons.

PRODUCTION, IMPORTS AND CONSUMPTION OF PYRITE IN THE UNITED STATES (a)
(In tons of 2240 lb.)

Year.	Production.		Imports. (b)		Consumption.	
1900.....	201,317	$684,478	322,484	$1,055,121	523,801	$1,739,599
1901.....	234,825	1,024,449	403,706	1,415,149	638,531	2,439,598
1902.....	228,198	971,796	440,363	1,650,852	668,561	1,622,648
1903.....	199,387	787,579	425,989	1,628,600	625,376	2,416,179
1904.....	173,221	669,124	413,585	1,533,564	586,806	2,202,688
1905.....	224,980	752,936	515,722	1,780,800	740,702	2,533,736
1906.....	225,045	767,866	597,347	2,138,746	822,392	2,906,612
1907.....	261,871	851,346	656,477	2,637,485	918,348	3,488,831
1908.....	206,471	744,463	668,115	2,624,339	874,586	3,368,802
1909.....	210,000	756,814	692,385	2,428,638	902,385	3,185,452
1910.....	223,700	830,150	806,590	2,773,627	1,030,290	3,603,777
1911.....	299,904	1,150,597	1,001,944	3,788,632	1,301,848	4,939,229
1912.....	350,928	1,334,259	964,478	3,860,738	1,315,406	5,194,997
1913.....	341,338	1,286,284	850,592	3,611,136	1,192,930	4,897,421
1914.....	336,662	1,283,346	1,026,617	4,797,326	1,363,279	6,080,672

(a) These statistics do not include the auriferous pyrite used for the manufacture of sulphuric acid in Colorado. (b) Net imports, less re-exports.
U. S. Geological Survey.

The domestic production of pyrite comes principally from the States of Virginia, California and New York, the States being named in the

order of their tonnage production. In addition pyrite is mined in the States of Georgia and Missouri and is obtained in the States of Illinois, Indiana and Ohio as a by-product of the coal-mining industry. Some pyrite is also produced in Wisconsin in connection with the zinc-mining industry.

WORLD'S PRODUCTION OF PYRITE
(In metric tons)

Year.	Belgium.	Bosnia.	Canada.	England.	France.	Germany.	Hungary.	Italy. (a)
1900	400	1,700	36,308	12,484	305,073	169,447	87,000	71,616
1901	560	4,570	31,982	10,405	307,447	157,433	93,907	89,376
1902	710	5,170	32,304	9,315	318,235	165,225	106,490	93,177
1903	720	6,589	30,822	9,794	322,118	170,867	96,619	101,455
1904	1,075	10,421	29,980	10,452	271,544	174,782	97,148	112,004
1905	976	19,045	29,713	12,381	267,114	185,368	106,848	117,667
1906	908	13,474	35,927	11,318	265,261	196,971	112,623	122,364
1907	397	3,671	35,494	10,357	283,000	196,320	99,503	126,925
1908	357	5,000	42,934	9,599	284,717	219,455	95,824	131,721
1909	214	(b)	58,645	8,564	273,221	198,688	98,971	149,084
1910	213	571	48,871	10,393	250,432	215,708	92,464	165,688
1911	122	3,118	74,978	10,276	277,900	217,459	96,754	165,273
1912	148	6,216	73,944	10,691	282,202	242,121	103,809	277,585
1913	268	3,242	207,532	11,611	311,167	(g)228,405	106,629	317,334
1914	.....	4,459	207,182	.....	.....	.....	.....	335,531

Year.	Japan.	Newfoundland.	Norway. (c)	Portugal. (c)	Russia.	Spain.	Sweden.	United States.	Total.
1900	16,166	*Nil*	98,945	402,870	23,154	34,638	179	204,538	1,464,512
1901	17,589	7,532	101,894	443,397	30,732	33,953	*Nil*	238,582	1,568,999
1902	18,580	26,000	121,247	413,714	26,465	145,173	*Nil*	231,849	1,713,654
1903	16,149	42,674	129,939	376,177	22,780	155,739	7,793	202,577	1,692,812
1904	24,886	61,166	133,603	383,581	31,667	161,841	15,957	175,992	1,696,099
1905	25,569	51,534	162,012	352,479	30,689	179,079	20,762	228,580	1,789,816
1906	36,038	28,583	197,886	350,746	20,660	189,243	21,827	228,646	1,832,475
1907	56,166	28,000	236,038	241,771	18,316	225,830	27,000	266,061	1,854,849
1908	33,867	(e)35,000	269,129	81,417	56,345	263,457	29,569	209,774	1,768,365
1909	27,066	*Nil*	282,606	284,735	46,078	236,000	16,104	213,371	(e)1,730,000
1910	78,418	*Nil*	322,000	312,906	55,980	294,184	25,445	227,280	1,826,854
1911	73,879	2,500	(e)350,000	282,773	113,054	344,879	30,096	304,974	2,348,035
1912	74,929	*Nil*	469,326	(f)601,443	123,990	421,070	31,835	356,707	3,076,016
1913	114,589	.....	441,129	(f)391,083	.....	926,913	34,319	347,027	3,441,245
1914	.....	.....	.....	.....	.....	.....	.....	342,273	.....

(a) Cupriferous in part. (b) Reports not yet available. (c) Both iron and copper pyrites. (e) Estimated. (f) Includes 120,148 tons copper iron pyrite in 1912 and 13,550 tons in 1913. (g) Prussia alone.

Foreign Pyrite Industry

Canada.—During 1914 there was exported from the Province of Ontario pyrite to the value of about $350,000, all of which went to the United States. Of the five companies producing pyrite in the province only one produced acid at the mine. More than one-half of the total production of the province was mined at North Pines in the Fort William district.

During 1915 it is estimated that Canada produced 296,910 short tons of pyrite valued at $1,028,678.

Norway.—The total pyrite produced in Norway in 1914 was about 430,000 tons which was taken from Sulitjelma, Stordoe, Bossmo, Foldal,

Roestvangen and Roros mines. Of this amount 358,114 tons were exported or about 70,000 tons less than during 1913. For home consumption about 60,000 tons were reserved and 42,852 tons of purple ore was exported. The Norwegian pyrite exported is estimated at about one-tenth of the total European shipments.

South Africa.—The possibility of pyrite mining as an industry in this country has had attention drawn to it at various times as a result of the demand for sulphur for the production of sulphuric acid, of which a considerable quantity is used in this country, mainly in the manufacture of explosives. We are not aware that any undertaking devoted solely to the production and sale of pyrite is existent in this country, except a small venture on the Black Reef, where it is said that a few people are engaged in concentrating the pyrite in tailings and selling it at a profitable figure to the Natal Ammonium Co. A little while ago a large number of claims were pegged out in the Low Country on an extensive series of pyrite-bearing quartzite, in which the sulphide was fairly abundant. An occurrence to the west of Pretoria has recently been taken in hand, also, in the vicinity of a farm where a small galena proposition has been worked with very satisfactory results for some months past. The pyrite here is said to occur in the massive form, the vein being of the interstratified kind which is commonly found in the Transvaal System. Some 13,741 tons of Sicilian sulphur were exported to South Africa during the same year. A figure of about £2 per ton has been quoted recently as the price which local buyers are prepared to pay for clean pyrite at present. The possibilities of an industry are obviously well worth looking into.[1]

Sulphuric Acid

It is a trite saying that sulphuric acid is to the chemical manufacturer what iron is in the metallurgical world. But to the general public this saying makes no appeal, for sulphuric acid is not a final product like iron, and is only a means to an end. It is not seen in our houses and highways, and to the average person it is merely a name, sometimes not even so much as that. To mining men it is more often than not a nuisance, as for instance in the case of smelter smoke or of acid mine-waters. Being a dangerous material and not conveniently stored and transported, it is usually manufactured on the spot where it is required, and manufacture precedes consumption by as short a space of time as possible. In other words, it is made according to requirements, and there is little acid on the market. It follows therefore that if a smelter is forced by the pressure of public opinion to make acid instead of pursuing the older and more

[1] *So. Afr. Min. Jour.*, Oct. 23, 1915.

convenient way of discharging the acid gases and vapors into the atmosphere, he is faced by a very real difficulty as regards the disposal of his by-product. He can rarely find a ready market for it, and has to create one by establishing a business that requires it as raw material. But if he can not sell his acid or use it in the manufacture of some more saleable article, he is in a serious quandary. The producer *malgre lui* is therefore in a difficult case. On the other hand, a consumer who suddenly wants an increased supply is in almost as bad a position, and his contemplated expansion of operations may be blocked for months. This feature of the trade is well exemplified by the large requirements of sulphuric acid needed for the manufacture of high explosives, on a stupendous and unprecedented scale, for the purposes of the present war. The shortness of shells and ammunition for the British army was due in large part to the difficulty of increasing the usual acid supply a hundred fold. While new factories were being built, the uttermost parts of the earth were scoured for ready supplies. Some was secured in the United States, and its shipment gave an instance of the difficulties of transport to which we have referred, for many of the containing vessels came to grief and did damage to the ships carrying them and to the other parts of the cargo.

Sulphuric acid has so many large industrial applications that we can not do more than indicate a few of them. The first of the big uses was the manufacture of soda products from salt by the Leblanc process, and consequently the acid works are usually found at the centers of alkali manufacture. Of recent years the introduction of the ammonia-soda and electrolytic processes has proportionately decreased the amount of acid used for this purpose. Similarly the amount of sulphuric acid consumed in connection with an adjunct of the Leblanc process, that is to say, the release of chlorine from bleaching powder at bleaching works, has suffered, seeing that nowadays much of the chlorine is supplied in liquid form instead of as bleaching powder; and moreover hypochlorites are used largely in bleaching, instead of free chlorine. Sulphuric acid is employed in the manufacture of most of the other acids. The list of commercially valuable salts of sulphuric acid is a long one, but we may specify as examples sulphate of ammonia and sulphate of copper. It is used in the production of soluble superphosphate from insoluble phosphate in bones and rocks, in the preparation from starchy materials of sugars used in brewing, in oil refining, in the production of aniline dyes and high explosives. All these manufactures call for large supplies of acid.

As regards the raw material from which the acid is made, Spanish pyrite still holds first place, and then comes native sulphur mined in Sicily and Louisiana. Other sulphides such as blende are employed, but

usually only when the acid is a by-product. The sulphur of the pyrite in coal is also an important raw material at gas-works, where the sulphur is caught by iron oxide, which is afterward sent to the acid plant. Much sulphur is also recovered from alkali waste and thus used over again. In the old days the acid was produced by the dissociation of green vitriol, or ferrous sulphate, a source that explains the origin of the name "oil of vitriol."[1]

The most important commercial grades of acid are the 50 B. or chamber acid, containing 62.18 per cent. H_2SO_4 and having a specific gravity of 1.526; the 60 B. acid or tower acid, containing 77.67 per cent. H_2SO_4 and having a specific gravity of 1.706. This grade also includes concentrated chamber acid or lead pan acid. The 66 B. or oil of vitriol contains 93.19 per cent. H_2SO_4 and has a gravity of 1.835. Besides these are the 97 per cent. monohydrate, and fuming acids which contain from 5 to 20 per cent. of dissolved trioxide.

About five-eighths of all the acid produced is chamber acid, the most of which is used in the manufacture of fertilizers from phosphate rock, the manufacture of sulphate of ammonia in connection with the destructive distillation of coal, and the manufacture of alum. Most of the 60° acid is used in the steel industry for pickling purposes; the 66° acid is principally employed in the purification of petroleum and in the manufacture of mixed acid in the explosives industry, as are also the higher strengths—the 97 per cent. and the fuming—the manufacture of reclaimed rubber and the general chemical industries.

The production of acid by grades is tabulated in detail below:

PRODUCTION OF SULPHURIC ACID IN THE UNITED STATES IN 1914 AND 1915, BY GRADES IN SHORT TONS
(Figures of the U. S. Gelogical Survey)

Grade.	1914.			1915.		
	Quantity.	Value.	Price per Ton.	Quantity.	Value.	Price per Ton.
50° Baumé	1,628,402	$9,712,056	$5.96	(b)1,518,271	$10,681,246	$7.04
60° Baumé	551,955	3,376,242	6.12	657,076	4,976,453	7.57
66° Baumé	916,192	10,509,471	11.47	1,019,024	14,211,381	13.95
Other grades	65,890	882,158	13.39	(c)189,795	2,787,971	14.69
Total	3,162,439	$24,479,927	7.74	3,384,166	32,657,051	9.65
Total reduced to 50° Baumé acid	(a)3,762,417	(a)24,163,331	$6.42	3,868,152	29,869,080	7.72

(a) Exclusive of 21,993 short tons of fuming acid, valued at $316,596. (b) Includes acid reported not only at 50°, but also as 52°, 53°, and 55°. (c) Includes stronger acid reported as oleum, etc., carrying varying percentages of free SO_3.

[1] *Min. Mag.*, Dec. 15, 1915.

PRODUCTION OF SULPHURIC ACID FROM COPPER AND ZINC SMELTERS, 1912–1915, IN SHORT TONS

(Figures of the U. S. Geological Survey)

Source.	60° Baumé Acid.								
	1912.			1913.			1914.		
	Quantity.	Value.	Price per Ton.	Quantity.	Value.	Price per Ton.	Quantity.	Value.	Price per Ton.
Copper smelters..	(b)321,156	b) $1,985,704	(b)$6.18	336,019	$2,205,627	$6.56	348,727	$2,215,690	$6.35
Zinc smelters....	(b)292,917	(b) 2,255,237	(b) 7.70	296,218	2,140,645	7.23	411,911	2,974,603	7.22
Total.....	(b)614,073	b) $4,240,941	(b)$6.91	632,237	$4,345,272	$6.87	760,638	$5,190,293	$6.82
Total acid reduced to 50° Baumé.	(c)764,237	.....	.....	790,296	.....	.....	950,798	.....	.....

Source.	1915.	Quantity.	Value.	Price per Ton.
Copper smelters, 60°.....	.....	360,522	$2,749,633	$7.63
Zinc smelters, 60°.....	.....	484,942	4,292,493	8.85
Other strengths.....	.....	59,189	579,115	9.78
Total.....	.....	904,653	7,621,241	8.42
60° acid reduced to 50° Baumé.....	.....	1,056,830	.....	.....

(a) The acid reported to the Survey includes that of strength of 50°, 53°, 60°, and 66° Baumé, and a small quantity of electrolyte and oleum. All strengths, with the exception of the electrolyte, have been reduced to both 50° and 60° Baumé, as given in the table.
(b) Inclusive of a small quantity of electrolyte.
(c) Exclusive of a small quantity of electrolyte.

The sulphuric acid industry in the United States in 1915 presented both remarkable and normal features. In spite of the abnormal demand, a great deal of sulphuric acid was consumed in the factories where it was made. The trade in strong acids was much more active on account of the demand for explosives and other war munitions, but this demand came only after the first quarter of the year and was very strong only during the last 6 months. Before that time some acid plants were shut down.

The production of sulphuric acid of 50°, 60° and 66° strengths in 1915 was 3,868,152 tons expressed in terms of 50° acid valued at $29,869,-080. In addition there was a production of 189,795 tons of fuming acid and oleum valued at $2,787,971. This is an increase of 3.5 per cent. in the three common grades, but the production of fuming acid and oleum increased to over eight times the 1914 figure. These figures include by-product acid produced at copper and zinc smelters amounting to 1,056,830 short tons of 50° acid. Compared with the production of 1914 this is an increase of 11 per cent. or 106,032 tons. The prices per ton of the stronger grades of acid, especially 60°, 66° and oleum during the last part of the year ranged far above those of 1914, and the total value of the output will therefore be in excess of what it was for that year.

An index of the development of chemical and metallurgical industry in Utah is found in the announcement by C. W. Whitley, general manager for the Utah department of the American Smelting & Refining Co., that his concern will shortly erect in the Salt Lake valley a sulphuric acid plant. It is reported that the manufacture of acid will be in conjunction with the smelting operations of the company, utilizing the sulphurous smelter gases. If the company's experiments in zinc hydrometallurgy with electrolytic deposition prove successful enough to warrant the construction of a commercial plant, much of the sulphuric acid produced will be used in the treatment of zinc ores.[1]

Exports.—Exports of sulphuric acid in 1915 were 77,812,029 lb., the largest on record. The total for 1914 and 1913 was 13,176,175 lb. and 9,689,005 lb. respectively. For the fiscal year of 1910 the total exports were only 5,081,038 lb. and in that of 1914 they were 12,131,750 lb.

Before the war 60° sulphuric acid sold at about $10.50 to $11 per ton in tank-car lots with $12 to $13 obtained for 66° acid. While as high as $110 is said to have been received for tank-car lots, some makers are now selling regularly at $40 to $45 for 60° acid in tank-car lots. Another producer is understood to be obtaining $75 per ton in tank-car lots and $80 per ton for acid in carboys for 66° acid. Commercial acid obtained as a by-product in zinc smelting is reported to be sold at $24 to $30 per ton.[2]

Nearly 3000 tons of sulphuric acid for making high explosives for use by the Allies is being shipped from Savannah every month to the du Pont Powder Works at Wilmington, and other manufacturers by Phosphate Mining Co., of Savannah.

This company has a contract with du Pont Co. that calls for nearly 150 tons monthly, and contracts with other companies fully as large. Officials state that contracts are good practically as long as the war lasts.

The sale of Anaconda's surplus output of sulphuric acid to du Pont interests is an unimportant transaction, so far as Anaconda is concerned. The bulk of output, about 125 tons a day, is used in its own plants. There was a small accumulation on hand, and this was sold. No firm contracts have been entered into for sale of this surplus product.[3]

Foreign Supplies

France.—The requirements of the French munition factories for sulphuric acid have become so important that it has been questioned whether the whole of the French output should not be reserved for the

[1] *Met. Chem. Eng.*, Feb. 1, 1916.
[2] *Min. Eng. World*, Mar. 18, 1916.
[3] *Min. Eng. World.*, Jan. 22, 1916.

state instead of the 20 per cent. as at present. Happily it has been remembered in time that the needs of agriculture are as important as others from the point of view of the war, and it has been finally decided to reserve the quantities necessary for the manufacture of superphosphate.

It is estimated that this will give from 300,000 to 400,000 tons of superphosphate—little enough in comparison with the amount used before the war, but now perhaps sufficient in view of the shortage of labor in the country districts.[1]

Great Britain.—Everywhere in England it is complained that the color difficulty grows greater, and the government consumption of sulphuric acid is freely given as the cause of the shortness of the supply of British-made colors. Dyers feel the shortage more acutely than anybody else, but the consequences are felt, of course, by everybody needing colored yarn or goods, so that there is a continual buzz of dissatisfaction. It may be hoped impartially that the arrangements for promoting the production of sulphuric acid are upon a scale commensurate with the new arrangements that are being made for its consumption. Very soon sulphuric acid will be wanted in quantities largely exceeding a consumption that is already tremendous, and a surplus beyond the needs of the explosives trade is indispensable if there are to be dyes in any abundance.[1]

Russia.[2]—During 1915 the Russian sulphuric acid business experienced very difficult conditions. The raw material for the production of the acid, and particularly sulphur ore, previous to the war was obtained from abroad to the extent of about three-quarters of the quantity required and only those factories in the east of the Moscow margin used Russian, usually Ural, pyrite. In addition to this the production of sulphuric acid takes place mostly in the western parts of European Russia, in some way or other having been affected by the military operations, so the seriousness of the question of supplying the industry, whether on behalf of the national defence or for private requirements can hardly be overestimated.

Technology

A new method of manufacturing sulphuric acid, for which advantages are claimed, is suggested in United States Department of Agriculture *Bulletin* No. 283, "The Production of Sulphuric Acid and a Proposed New Method of Manufacture." The essential difference of the method is that the gases employed are drawn downward through a spiral flue in place of being drawn through lead chambers or intermediate towers. It is asserted that the resistance of gases to the downward pull and the constant change in their course through the spiral tend to mix them very

[1] *Eng. Min. Jour.*, December, 1915.
[2] *Chem. Trade Jour.*, Apr. 1, 1916.

intimately. The fact that the gases constantly impinge on the walls of the spiral flue, which can be cooled either by air or water, makes it practicable to maintain the gases at a temperature most favorable for the efficient yield of sulphuric acid.

In laboratory tests in which the spiral was utilized practically all the sulphur dioxide was oxidized to sulphuric acid, only traces being lost through escape or in the system. The lead spiral, the author points out, however, is not intended to replace the Glover tower, nor to do away with the Gay-Lussac tower.

It is believed that while the lead spiral will take considerable lead, the great reduction it will effect in the chamber space will make it possible to construct a plant with considerably less lead than is required in the ordinary chamber system.

The new type of plant requires no other device to accelerate the reactions, occupies much less ground space, and would not need as large buildings, and therefore should decrease the initial cost of construction. The method, however, has been tried only on a laboratory scale, and the bulletin refuses to predict just how efficient the commercial plant would be, but states that all indications are that this method offers promise of being economically successful.[1]

New Use.—At one of the sessions of the recent San Francisco meeting of the American Institute of Mining Engineers, Dr. Lippman explained the nature and results of his investigations, and illustrated by photographs the apparent beneficial results obtained by applications of sulphuric acid to alkali soils. The views showed crops growing on test plots that had received from 2½ to 7½ tons sulphuric acid per acre, the ground being otherwise unfit for agricultural purposes on account of the concentration of alkali salts. One effect of the acid is to cause a shrinkage of the colloids, giving a better opportunity for aeration of the soil and circulation of moisture, and creating more favorable conditions for the activity of nitrifying bacteria.

An important feature of the work from the metallurgical standpoint is the quantity of acid used, running into tons per acre. From the agricultural side there is prospect of rendering useful a vast acreage of ground in the Western States, now lying waste and shunned by the farmer. Here is prospect of coöperation for mutual good between interests that have regarded each other with suspicion and enmity.[2]

Sulphuric Acid Substitutes[3]

A small committee of users of sulphuric acid in the Yorkshire, West Riding, England, along with a representative of the Ministry of Muni-

[1] *Comm. Rept.*, Sept. 22, 1915.
[2] *Met. Chem. Eng.*, Oct. 1, 1915.
[3] *Chem. Trade Jour.*, Jan. 8, 1916.

tions and officials of the West Riding of Yorkshire Rivers Board, have been considering how to overcome the difficulty in which they are placed by the scarcity of sulphuric acid. The conclusions arrived at are the subject of the following report made by the Secretary to the Committee:

For some time past the supply of sulphuric acid has fallen much below the demand, and recently the Ministry of Munitions have made it known that they will require greatly increased amounts for the manufacture of explosives, so that the supply for ordinary manufacturing purposes will shortly be still more reduced. It is necessary, therefore, to inquire whether any substitutes can be obtained, and such a substitute there is in niter cake, a by-product from the manufacture of nitric and sulphuric acids.

Niter cake is produced at present in such enormous quantities that some makers have been compelled at great expense to find spoil heaps upon which to deposit it or to carry it out to sea and dump it there. This is an extremely wasteful proceeding, inasmuch as the cake contains the equivalent of some 30 per cent. of pure sulphuric acid, which is quite available for many of the processes in which sulphuric acid is used in ordinary times. Experiments in the use of niter cake have been carried out at a number of mills in the West Riding in connection with the various operations in which sulphuric acid is ordinarily used: (*a*) For the extraction of grease from piece-scouring suds. (*b*) For the extraction of grease from wool suds. (*c*) For the refining of grease. (*d*) For stripping color from rags in the making of shoddy. (*e*) For extracting cotton from mixed fabrics in the shoddy trade. (*f*) For dyeing rags in the shoddy trade.

From the results of these experiments, which have all been on a working scale, it is evident that niter cake can be used in place of ordinary sulphuric acid for the extraction of grease, either from wool suds or piece-scouring suds, for the refining of grease, for the stripping of rags except for perhaps where light dyes are to be subsequently used, and for dyeing rags in the shoddy trade, more especially where dark colors are being used.

In using the niter cake for extracting cotton from rags, grave difficulties have presented themselves, but even in this case it would appear that niter cake can be to some extent substituted for sulphuric acid. The use of niter cake presents certain difficulties, but these for the most part can be surmounted.

1. It is more difficult to handle than acid, since it is in the form of solid cake, and must be used in larger quantities, as it contains only 30 per cent. of its weight of pure sulphuric acid, compared with the 75–80 per cent. present in acid.

2. In carriage, storage, and handling, the acid liquid draining from it causes damage which may be serious.

3. The great difficulty, however, is that of transporting it either by railway or by road, and this is enhanced by the greater amounts necessary.

The best method of using the cake is to dissolve it in hot water by the aid of steam, and to use this solution while still hot. The solution in an equal weight of water usually contains one-sixth of the sulphuric acid, and therefore must be used in quantities about six times greater than when acid is used.

The cake can be stored with safety by placing it under cover on an asphalted floor, or on a stone floor the joints of which are sealed with asphalt, drained to a catch-pit, where any acid can be caught for use. Care should be taken that the acid draining away is not allowed to penetrate into the soil near any buildings. It is desirable to have as little handling of the cake as possible, as it is as dangerous a substance as ordinary acid, and the men working with it should have their clothes protected by sacking, and should be provided with oil or grease to protect their hands.

The chief difficulty to be met is that of railway carriage and cartage, and if niter cake is to be generally used in place of acid, very large quantities will have to be conveyed by rail and road. In this direction the assistance of the Ministry of Munitions has been asked. It is suggested that arrangements should, if possible, be made for depots to be established at certain centers, *e.g.*, Bradford, Dewsbury, Huddersfield, Keighley, Leeds, and Wakefield, at which the cake may be dumped in large quantities and from which it may be distributed by carts or motor trucks. To such depots regular trains could be kept running from the producing centers.

The difficulty of local cartage is as great as that of carriage by railway, and the Ministry have been asked to consider the question of making some arrangements for securing the necessary supply of carts and motor trucks. It is necessary to point out that the introduction of niter cake, if it is to be substituted for sulphuric acid on a large scale, will entail a sudden and great disorganization of many of the operations in the woolen trade and several trades in the West Riding are equally concerned. It is suggested, therefore, that to deal with the various difficulties which must arise, a large and representative committee should be formed by the Ministry, consisting of users of sulphuric acid in the West Riding.

A representative committee of this kind would be found useful in disseminating information, in helping the manufacturers to use niter cakes to the best advantage and in advising the Ministry of Munitions

on any difficulties which may arise, especially in regard to the proper distribution of niter cake and of the sulphuric acid that may be available.

To prevent manufacturers of niter cake unduly inflating prices, the Ministry have arranged to dispose of a very large amount produced at His Majesty's factories at Queensferry, Cheshire, at Oldbury, and at Gorton Brook, free on rail or at a nominal charge and as other huge amounts are produced at factories in the neighborhood of the Thames, where the niter cake is at present disposed of at considerable cost, it is possible that further arrangements of this nature can be made, and that in these cases, the manufacturers or the Ministry may be induced to pay part of the cost of the carriage.

The matter is one which interests the Rivers Board very closely, inasmuch as the suds from piece scouring and wool washing are required to be treated with acid for their purification, and the Board have instructed their officials to give any information in their possession to any of the manufacturers who may desire to make use of niter cake, or who meet with any difficulties in its use.

Bibliography

Sulphur

Anon.—The Copper and Sulphur Ore Industry in Norway. *Eng.*, **90**, 46–7.

Anon.—The Sicilian Sulphur Industry. *Comm. Rept.*, Aug. 18, 1915.

Bargagli-Petrucci, G.—A Biological Hypothesis on the Deposition of Sulphur during the Chalk-Sulphur ("Gessosso-solfifera.") *Epoch. Atti. accad. Lincei*, **24**, 1, 631–8.

Doak, S. E.—Rotary Kilns for Desulphurization and Agglomeration. *Bull. Amer. Inst. Min. Eng.*, 1915, 2061–66.

Hunt, W. F.—The Origin of the Sulphur Deposits of Sicily. *Econ. Geol.*, Sept.,–Oct., 1915, 543.

Lindt, V.—The Bad Influence of Sulphide and Sulphate Sulphur on the Reduction of Roasted Blende. *Metall u. Erz*, **12**, 335–47.

Martin, A. H.—Treating Sulphurous Fumes at the Mammoth Smelter. *Met. Chem. Eng.*, **12**, 769–70.

Miege, E.—The Question of Sulphur in Agriculture. *Rev. Sci.*, **52**, 778.

Pagliani, S.—Internal Temperatures of Sulphur Furnaces. *Ann. Chem. Applicata*, **4**, 75–81.

Pellet, H.—Note on the Use of Washers and Coolers with Sulphur Ovens, and on the Sulphuric Acid Content of the Oven Gases. *Internat. Sugar Jour.*, **16**, 465.

Perrier, C.—Sulphur from Zonda, Argentine. *Atti. accad. Lincei*, **24**, 1, 622–5.

Wierum, H. F.—The Hall Process of Desulphurization. *Met. Chem. Eng.*, **12**, 718–21.

Zanker, W., and Farber, E.—Formation of Sulphuric Acid from Sulphur. *Farber Ztg.*, **25**, 343–5; 361–2.

Pyrite

Barth, S.—The "Bracq-Moritz Furnace" for Roasting Pyrites and Similar Material. *Chem. App.*, **2**, 95–6.

FALKENBURG, O.—The Geology and Petrology of the South Norway Pyrite Deposits with Special Reference to Their Origin. *Zeit. Prakt. Geol.*, **22**, 105.

PILZ, R.—Note on the Genesis of the Huelva District Pyrite and Manganese Ore Deposits. *Zeit. Prakt. Geol.*, **22**, 373–7.

v. REITZENSTEIN, W. F.—The Gross-Fragrant Pyrite Deposits. *Zeit. Prakt. Geol.*, **22**, 197–212.

STOREN, R.—Notes on Pyritic Smelting. *Metall u. Erz*, **12**, 200.

UDHANY, A. D.—The Grong Copper and Pyrite Mines of Norway. *Eng. Min. Jour.*, **99**, 889–92.

YOUNG, R. B.—Note on Pyritic Concretions in Karroo Sandstones. *So. Afr. Jour. Sci.*, **11**, 147.

SULPHURIC ACID

ANON.—Modern Sulphuric Acid Plant. *Chem. Trade Jour.*, Aug. 7, 1915.

ANON.—Transportation of Dangerous Articles on Vessels. *Comm. Rept.*, 158 (1915).

ANON.—Sulphuric Acid in Germany. *Chem. Trade Jour.*, Nov. 27, 1915.

ANON.—Construction of Sulphuric Acid Plant. *Salt Lake Min. Rev.*, Dec. 15, 1915.

DURON, A. G.—Concentration Apparatus for High Percentage Sulphuric Acid. *Zeit. angew. Chem.*, **27**, 1, 568.

HITIER, H.—Employment of Sulphuric Acid in Fields of Cereals. *Jour. agr. prat.*, **28**, 347–8.

HOFFMAN, A.—The Impurities of Metallurgical Chamber Acid. *Metall u. Erz*, **12**, 290–7.

KAUSCH, OSKAR.—Modern Sulphuric Acid Concentrators. *Chem. app.*, **1**, 257–60.

KAUSCH, OSKAR.—Innovations Relating to Lead Chambers, Tower Systems and Other Apparatus for the Manufacture of Sulphuric Acid. *Chem. app.*, **2**, 53–55.

MARSHALL, A. E.—Fused Silica Dishes for the Concentration of Sulphuric Acid. *Met. Chem. Eng.*, **13**, 136–7.

MASON, W.—Apparatus for Condensing Sulphuric Acid. *Met. Chem. Eng.*, **13**, 17.

MATHEWSON, E. P.—New Anaconda Leaching and Acid Plants. *Eng. Min. Jour.*, **99**, 723–7.

REUSCH, K.—Effects of the War on the German Sulphuric Acid Industry. *Chem. Ztg.*, **38**, 1241–3.

SCHLIEBS, G.—An Innovation in Sulphuric Acid Tower Systems. *Chem. Ztg.*, **38**, 966.

WAGGAMAN, W. H.—The Production of Sulphuric Acid and a Proposed New Method of Manufacture. *U. S. Dept. Agr. Bull.*, **283**.

WENTZKI, O.—Theory of the Lead Chamber Process. *Zeit. angew. Chem.*, **27**, 1, 512.

WALKER J.—Development of the Contact Process for the Manufacture of Sulphuric Acid. *Jour. Soc. Chem. Ind.*, **24**, 1123.