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CHROMIUM

BY

DAVID T. DAY

ABSTRACT FROM "MINERAL RESOURCES OF THE UNITED STATES,
CALENDAR YEARS, 1883 AND 1884"—ALBERT WILLIAMS, JR.,
CHIEF OF DIVISION OF MINING STATISTICS



WASHINGTON
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1885

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CHROMIUM.

BY DAVID T. DAY.

History of the chromium industry.—Just as the industry of nickel and cobalt has been developed entirely in one locality, Camden, New Jersey, so the chromium industry has found its development entirely in the neighborhood of Baltimore, Maryland, and one firm has been instrumental in bringing it to its present condition, although the industry has spread to the Pacific coast, and the firm has reached the fourth generation. About sixty years ago it became known to Mr. Isaac Tyson that chrome iron ore occurred on his farm at Bare Hills, Baltimore county, Maryland. His son, also named Isaac Tyson, who was engaged in the mining business, began working out the ore and shipped it to England. In 1833 he entered into an agreement with an Englishman of reputed scientific ability to begin the manufacture of paints, for which the chrome ore was decomposed and transformed into various pigments. The knowledge of the Englishman proved inadequate, and the venture was not successful. Mr. Tyson, although actively engaged in business pursuits, then began to study the various processes for working up chrome ore and similar substances, supplying the want of scientific training by most assiduous study of the scattered literature which France and other countries could furnish relative to such subjects. Meanwhile chrome ore was again shipped to England, this being the only demand for it until about 1843. The deposits at Bare Hills never furnished much ore; they were rapidly exhausted, and, the trade with England being once started, inquiry was made for new deposits. Wherever ore was reported it was at once investigated, and, if valuable, controlled by Mr. Tyson. In this way ore was discovered and worked out in large quantities at Soldier's Delight, Baltimore county. In Harford county an enormous deposit was found which furnished ore steadily for more than forty years. In Cecil county ore was again found, and another large deposit at Wood's mine, Lancaster county, Pennsylvania. When this deposit and others in Delaware and Chester counties were reached, Mr. Tyson feared that more mines might be discovered than could be operated by himself, the English market might become overrun with ore and leave no sale for his own product in Maryland. To make an independent market, therefore, for his ore, Mr. Tyson again applied his study to manufacturing, and with such phenomenal success that the works established in 1845 for utilizing chrome ore still monopolize the chromium industry in the United States. At first the yearly amount of chromium

salts made was insignificant, but gradually they replaced the importation from England, until finally the Baltimore chrome works supplied this country entirely.

The secret of success in the "Tyson works" lies in some unpublished feature of their method of decomposing chrome iron ore. This substance resists the action of most chemical agents to an exceptional degree. Until the year 1820 chrome iron ore was decomposed by roasting with potassium nitrate (niter). In that year Köchlin introduced certain chromium salts in the process of Turkey-red dyeing, and they soon were employed for a variety of purposes, especially in connection with dyeing wool. The increased consumption led to improvements in the decomposition of the ore, and potassium carbonate was introduced in the manufacture, instead of potassium nitrate; the oxidation was effected by atmospheric oxygen in reverberatory furnaces. About the year 1845 an important improvement was made by Stromeyer in the introduction of a certain quantity of lime together with potassium carbonate. Not only was a saving of alkali effected, but the oxidation was rendered easier, inasmuch as the whole mass did not fuse, and therefore remained porous and more capable of absorbing the atmospheric oxygen. (a) As at present understood, therefore, the decomposition of chrome ore consists in powdering the mineral by means of good millstones, heating it for some hours in a reverberatory furnace with potassium carbonate and lime in certain proportions, and dissolving out the chromium from the fused mass by water, in the form of potassium chromate, which is converted into bichromate by sulphuric acid. This operation is put down in the text books as comparatively simple; but in the past twelve years no less than fifteen attempts have been made to establish works for decomposing chrome ore, in Philadelphia, New York, and Boston. It is, however, an extremely difficult matter so to regulate the manufacture as to produce potassium bichromate at the present market price. This, by long experience and devices known to itself, the Baltimore firm is able to do.

Domestic sources.—Chromium is found in irregular deposits in several widely separated districts in the United States. Its presence is usually indicated by the associated serpentine rock. The two districts which have an important bearing on the industry are located one in Maryland and Pennsylvania and the other in California. Of these the Maryland district begins in the Green Spring valley, in Baltimore county, and extends through Harford and Cecil counties, ending in Lancaster, Delaware, and Chester counties, Pennsylvania. In this district the deposits occur irregularly through the counties named. Bare Hills and Soldier's Delight, near Owen's Mills, in Baltimore county, have furnished somewhat more than 5,000 tons of sand ore. Reed's mine, in Harford county, furnished over 100,000 tons. Wood's mine, in Little Britain township,

a Roscoe and Schorlemmer's Treatise on Chemistry, Vol. II., part 2, page 171.

Lancaster county, Pennsylvania, is an old and well-known deposit, from which considerable ore has been sent to Baltimore. Low's, Line-pit's, and Jenkins's mines are also noted deposits, in Fulton township, Lancaster county. In Chester county chromium is found in Elk and Nottingham townships. It is also found in Middletown and Marple townships, Delaware county, Pennsylvania.

A few isolated occurrences of chromium ores have been noted, though not mined, in States north of the Maryland district: in New York, at Phillipstown, Putnam county, and at Wilke's mine, Monroe, Orange county; in Massachusetts, in Blandford and Chester townships, Hampden county; in Vermont, in Jay, Troy, and Westfield townships, Orleans county.

South of the Maryland district chromium is found in Virginia, at Drainesville, near the Potomac, in Fairfax county. Quite recently a deposit of chrome ore was reported in Jackson county, North Carolina, which, as stated in the last report, promised to yield ore of better quality than any other in the eastern States. The deposit has not, however, been worked up to the present. Chrome ore is known to occur in small quantity in North Carolina, in Guilford county; at Cullasaja, Higdon's, Elijay's creek, and Moore's mine, Macon county, and in Yancey, Clay, Mitchell, Burke, and Watauga counties.

Until about three years ago, the Maryland district included in it nearly all the mines from which chromium was obtained, but since then an entire change has been made in the supply. The eastern mines have been practically abandoned, and now all the ore comes from the more recently discovered deposits in California. Fifteen years ago Messrs. Tyson & Sons were informed by their attorney in West Chester, Pennsylvania, that his brother, living in Del Norte county in the extreme northwestern part of California, had discovered chrome ore on his farm. About this time Mr. Simpson, a Baltimore merchant, urged the Tysons to aid him in working gold mines of reported immense value in Arizona. A surveyor was sent by the Tysons to Arizona with Mr. Simpson to investigate the supposed gold deposits. They proved worthless, and after Mr. Simpson had been killed by hostile Indians, the surveyor thought it best to investigate another region and examine the reported chromium deposits in California. They proved to be hornblende rock without value, but by a mere accident, which has always been a feature of chromium discoveries, he found a large deposit of chrome iron ore in another part of the county. For some years past the deposit has been worked and large quantities of ore have been extracted by the Tyson Mining Company, and as yet there are no signs of exhaustion in this field. Following the discovery in Del Norte county came that of ore in Sonoma, San Luis Obispo, and Placer counties; and chromium is now known to be common throughout California, having been noticed in more than half the counties of the State. The unde-

veloped deposits and mere croppings are, in fact, too many to admit of their enumeration here. Chromium also occurs elsewhere on the Pacific coast, but to what extent or of what quality has not been determined, no attempts at utilizing it having been made except in California, where it has been mined and shipped to eastern markets at the rate of about 3,000 tons per year since its discovery. The deposits in California most entitled to notice, because of their magnitude, good grade, or the extent to which they have been worked, are the following: Near Litton Springs, Sonoma county, from which there were extracted some years ago about 2,000 tons of ore, cost of mining and delivering at San Francisco about \$4.50 per ton, average price obtained about \$9 per ton; Sow Divide copper mines, Del Norte county, from which there were taken some years ago several thousand tons of good chrome ore—no work has been done there lately; Campo Seco, Calaveras county, a good article and in large quantity. This last-named deposit can be worked to good advantage when the narrow-gauge railroad now in course of construction shall reach Campo Seco. In San Diego gulch, in the same county, there is said to be an isolated mass of chrome iron that will weigh thousands of tons. From the chrome mines of San Luis Obispo county the largest amount of ore has been shipped, the total exceeding 15,000 tons. This was a number of years ago, no shipments having been made lately from that county owing to the low prices of chrome ore. Most of the chrome now being extracted in California comes from Placer county, from which shipments have averaged in 1883 and 1884 about 2,000 tons per annum. Just now this industry is much depressed in California, but with prices slightly improved it would more than regain its former activity. All of the sources utilized are as a rule worked by the Tyson Mining Company. Other companies are also engaged in the work of extracting ore in a small way. It is taken by wagons to the nearest railroad and transported to San Francisco. If not already the property of the Tysons it is all bought by them and shipped in sailing vessels by way of Cape Horn to Baltimore. A small amount is exported.

At present there is no indication of exhaustion in the California mines, and yet every effort is being made to discover new deposits, for the reason that these deposits are not found in veins or leads from the direction of which new mines can be predicted, but in isolated pockets of all sizes, sometimes yielding only a few pounds and sometimes many thousand tons. The miner is never sure but that the next day may find his deposit exhausted or the quality of the ore no longer profitable. The only rule that has been found is that the ore is richest at the surface and decreases in value as the mine become deeper. The value of a mine decreases very rapidly with the depth; for, in addition to the cost of getting ore to the surface and of keeping out water from the mine, the ore contains less chromium. The mines in the eastern States

are by no means exhausted; the reason why the California ores have been substituted is because they are nearer the surface and therefore richer. As the cost of grinding and decomposing the ore is the same for rich as for poor grades the rich ores are more profitable; moreover the higher the percentage of chromium in the ore the easier is its decomposition.

The general results of over one hundred analyses of ore found in California may be given as follows:

	Chromic oxide.
	<i>Per cent.</i>
Del Norte county	39 to 45
Napa county	42 to 46
Placer county	35 to 55
Tuolumne county	44 to 45
San Luis Obispo county	38 to 60
El Dorado county	20

Foreign sources.—Ores of the same character as those of California are found in Turkey, Russia, and Asia Minor. From this last source a small quantity of ore annually finds its way to Baltimore. The amount, however, is small and irregular. Nearly all the ore which supplies the Scotch and French manufactories of chromium salts comes from Russia. The ore is mined in Siberia and transported to St. Petersburg on rafts down the various watercourses. These rafts start on their journey in the spring, are frozen up all of the next winter, and reach their destination the second summer. The rafts are sold for lumber and the ore is shipped to England. By this means ore is mined in a remote region at small expense; without this cheap system of rafting competition with American ores would be impossible.

Character of the ores.—Chromium occurs as a constituent of several minerals. Cröcoite, for example, is chromate of lead; the green color of the emerald is due to traces of chromium; while penninite, chromic mica or fuchsite, and other minerals owe their color to this metal. But the ore from which chromium is always obtained is chromite or “chrome ironstone.” Its composition may be expressed by the formula $FeCr_2O_4$; but part of the chromium may be replaced by iron, or the iron may be partly replaced by magnesium, and the replacements are found in ore far removed from the surface of the ground. Aluminum is also sometimes present, and silica is often found in the sand ore, or ore containing the chromite in the form of small grains. The purest ore is found in lumps weighing sometimes several pounds.

Production.—The following table represents about the amount of ore mined in the last three years; it is all from California:

Production of chrome ore in California.

Years.	Tons of 2,240 pounds.	Value in California.
1882.....	2,500	\$50,000
1883.....	3,000	60,000
1884.....	2,000	35,000
	7,500	145,000

There is no regular spot value for chrome ore at the mines, as the cost varies irregularly in each district and much is mined by the manufacturers' agent who owns the mine. In San Francisco the ore is worth from \$18 to \$20 per long ton. By the time it reaches Baltimore the cost is from \$35 to \$40 per long ton. The total amount expended therefore for chrome ore in 1883 and 1884 was about \$190,000.

Exports.—The value of ore exported from 1864 to 1883 is given in the following table.:

Value of chrome ores exported from the United States, 1864 to 1883 inclusive.

Fiscal years ending June 30—	Value.
1864.....	\$39,585
1865.....	19,078
1873.....	2,080
1874.....	4,288
1880.....	7,540
1882.....	1,548
1883.....	2,905
1884.....	(a)

a None reported.

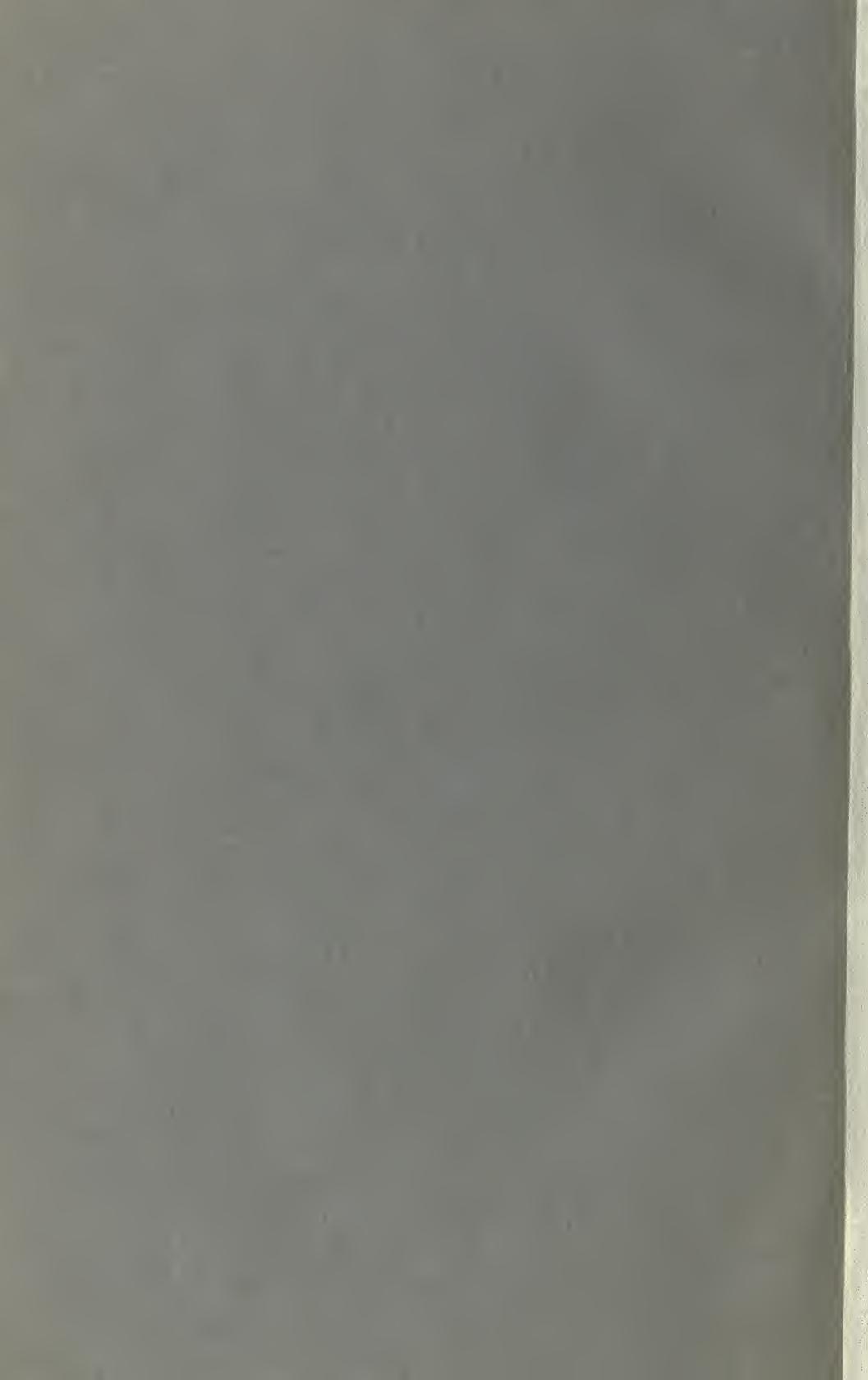
Utilization.—Nearly all of the chrome ore used in the United States is made into potassium bichromate by Jesse Tyson & Sons, at Baltimore. About 50 tons a year is made into chrome steel at the Brooklyn Chrome Steel Works. Potassium bichromate is therefore the one salt from which all other compounds have been obtained. The amount of potassium bichromate produced in the United States is in all about 1,500 tons a year. Of this, a small quantity, amounting to about 250 tons a year, is made by Harrison Bros., who have been making bichromate for about three years past at the branch of their color works called the Kalion Works, Philadelphia.

Imports.—Besides the domestic product about 1,000 tons of bichromate are annually imported from Scotland under a duty of 3½ cents per pound. Chromic acid, which is obtained from the bichromate, is also imported in small amounts; it would probably become a more extensive article of commerce except for the danger of its setting fire to vessels and storehouses. The following table gives the actual amounts imported and their value from 1867 to the end of the fiscal year 1884:

Chromate and bichromate of potash and chromic acid imported and entered for consumption in the United States, 1867 to 1884 inclusive.

Fiscal years ending June 30—	Chromate and bichromate of potash.		Chromic acid.		Total value.
	Quantity.	Value.	Quantity.	Value.	
	<i>Pounds.</i>		<i>Pounds.</i>		
1867	875, 205	\$88, 787	\$88, 787
1868	777, 855	68, 634	68, 634
1869	877, 432	78, 288	\$3	78, 291
1870	1, 235, 946	127, 333	8	127, 341
1871	2, 170, 473	223, 529	5	223, 534
1872	1, 174, 274	220, 111	514	49	220, 160
1873	1, 121, 357	178, 472	922	276	178, 748
1874	1, 387, 051	218, 517	44	13	218, 530
1875	1, 417, 812	183, 424	45	22	183, 446
1876	1, 665, 011	175, 795	120	45	175, 840
1877	2, 471, 669	264, 392	13	10	264, 402
1878	1, 929, 670	211, 136	32	35	211, 171
1879	2, 624, 403	221, 151	221, 151
1880	3, 505, 740	350, 279	5	3	350, 282
1881	4, 404, 237	402, 088	124	89	402, 177
1882	2, 449, 875	261, 006	52	42	261, 048
1883	1, 990, 140	208, 681	290	338	209, 019
1884	2, 593, 115	210, 677	120	210, 797

Sodium bichromate.—On account of the less cost of sodium carbonate it has frequently been proposed to substitute it for potassium carbonate in the decomposition of chrome iron ore, and thus produce sodium bichromate instead of the potassium compound. There are several obstacles to this: The decomposition is not as readily affected with sodium carbonate as with potash, and, further, sodium bichromate is by no means as easy to crystallize as the potassium salt, and in fact it is with great difficulty that sodium bichromate can be crystallized at all. But about three years ago the manufacture of sodium bichromate was introduced by German chemists, and the effect on the industry can already be seen. Before this German innovation, factories in Scotland and France supplied Europe with chromium salts. The introduction of sodium bichromate has brought about competition with Germany, amounting to a chromium war. The Scotch and German manufacturers are trying each to drive the other from the field. In 1882 the price of potassium bichromate was 15½ cents per pound. In 1883 it fell to 12 cents, and it now is selling in this country at 10½ cents, the lowest price it has ever reached. What the outcome of this competition may be can be surmised from the fact that within the last few months the Baltimore firm has begun the manufacture of sodium bichromate, though only as an experiment so far. For many purposes sodium bichromate can take the place of the potassium salt without disadvantage. For example, in any use where the oxidizing action of the salt is the only point to be considered, as in the manufacture of Turkey red, or alizarine, one salt is as useful as the other. The most important application of potassium bichromate in the arts is for calico printing. For this purpose dyers prefer potassium bichromate to sodium bichromate. In how far this is mere prejudice it is not possible to say. In the manufacture of pigments, in which bichromates find application for making “chrome yellow,” “chrome orange,” and “chrome green,” either salt can be used.



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