8-24-48

Manufacture of Potassium Permanganate
at Investigation by I. G. Farbenindustrie

E. Litherland
Butterfield

W. Müller of the above organization wrote the informative chapter on manganese salts in the 1940 Winnacker-Weingaertner Chemical Technology, Volume "Anorganische II", pages around 497-512. Mr. Glevis Adams did research on this topic for The Sherwin-Williams Co. during the war when we needed to manufacture our own potassium permanganate etc, and he says that it was a difficult and not wholly satisfactory undertaking, and he wants Müller's article carefully preserved in our files against the day that we may need to undertake permanganate manufacture again. He says that the only man in the United States with the know-how is Gerns, proprietor of the permanganate factory at LaSalle, Illinois. Adams also says that we should consider, in conjunction with our present examination of the manufacture of chromic oxide from bichromates, whether such a plant might serve a dual purpose, sometimes manufacturing permanganate. He also wants noted in the file on the manufacture of bichromates, which we are now considering, that a bichromate furnace plant might at the same time be a permanganate furnace plant. A fresh look at such problems also calls up the following thoughts: Would manganate suffice, --- is permanganate needed, in the removal of iron and manganese from zinc sulfate liquor, and would osone, a reagent famously easy to use for such a purpose, be now sufficiently easy to supply that no manganese compounds would be needed. What about hydrogen peroxide or other peroxides, much more available and cheap since the war? Following is a detailed abstract of Müller's article in Winnacker-Weingaertner, insofar as the manufacture of potassium permanganate is described:

MnO_2 plus 2 KOH plus KNO$_3$ 1/2 O_2 gives K_2MnO_4 plus H_2O

$2K_2MnO_4$ plus $2CO_2$ gives $KMnO_4$ plus MnO_2 plus 2 K_2CO_3

or $2K_2MnO_4$ plus Cl_2 gives 2 $KMnO_4$ plus 2KCl

or $2K_2MnO_4$ plus O_3 (ozone) gives$KMnO_4$ plus K_2O plus O_2

or K_2MnO_4 plus H_2O plus F (fluorine) gives $KMnO_4$ plus KOH plus 1/2 H_2F_2

Ashmanoy and Klemenuk, Z. Elektrochemie, 1910, pp 104 ff and 170 ff, concluded as a result of their research that according to the equations
MnO_2 plus KNO$_3$ plus 1/2 O_2 gives K_2MnO_4 plus H_2O

and K_2MnO_4 gives, reversibly, K . O^2 . KOH (p 1/2 O_2)/p p H_2O)

that the best possible output will be obtained if the quotient p 1/2 O_2/ p H_2O is kept large as possible, that is, the oxidation be done with the smallest possible water partial pressure and the highest possible oxygen partial pressure. They offer the opinion that in air the optimum temperature is about 600°C. At 550°C they observed diminished output, which they ascribed to the dissociating effect of the water liberated from the alkali:

MnO_2 plus 2 KOH plus 1/2 O_2 gives K_2MnO_4 plus H_2O
$2MnO_4$ plus 2 KOH gives 4 KOH plus Mn_2O_3 plus 1 1/2 O_2

and at the same time the charge sintered, slowing or preventing the further ingress of oxygen and the formation of manganate.

Based on these findings they proposed to make a preliminary melt and hold it at 200-250°C until all water vapor was expelled, then grind it well and heat it at 500-600° C in air.

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Schmidt, Ber. 43, 891 and 448 (1911) studied the effect of alkalies on MnO_4 (must mean K_2MnO_4) in fusions and concluded that there is formed under the conditions $8K_2O \cdot Mn_2O_7$, that is, $8K_2MnO_4 \cdot 2K_2MnO_3 \cdot 8K_2O$, which reacted with 5 H_2O to give $3K_2MnO_4$ plus 2 MnO_2 plus 10 KOH

Schlesinger, Whalbinix & Popoff, Ind. Eng. Chem. 11, 317 (1919) and Schlesinger, Jackson & Cardray, ibid., 13, 53 (1921), then ascertained that good yields were obtained in a moist air stream if to the MnO_2 mineral there was taken 1 mole MnO_2 to 2.5 moles of KOH. 2.2 moles of KOH sufficed for precipitated MnO_2 hydrate. Excess KOH reduced the K_2MnO_4 output due to formation of manganate-manganite. The reaction is strongly dependent on temperature in the sense that the formation of manganate-manganite increases with increasing temperature. Good temperature is 225-270°C. At 415°C only 60% output is obtained. The presence of water vapor is requisite. In dry atmosphere the formation of manganate ceases.

The author, Miller, explains these observations by subscribing to an intermediate manganate-manganite formation, perhaps that of Schmidt. The potassium manganite is readily converted to manganate by atmospheric oxygen. (We must mean that this happens as the first-formed double salt decomposes).

The I. G. Farbenindustrie plant at Bitterfeld has studied the effects of varying atmospheric moisture and varying added steam. These studies have shown that at any given molecular ratio of MnO_2 to KOH the speed of formation of the manganate is extraordinarily dependent on the partial pressure of H_2O vapor in the air used, in the sense that with increasing partial pressure the speed of oxidation attains a maximum and then diminishes with still greater H_2O partial pressure as the region of manganate decomposition is reached. Thereat water participates in the reaction. At first compounds of K_2O and MnO_2 hydrates are formed. Depending on the conditions these hydrates will either, (1) decompose into complexes of lower or zero water content which cannot under the conditions be oxidized to manganate, or (2) with sufficiently high H_2O partial pressure readily become manganate. Reactions (1) and (2) take place side by side at the same time. It has not been definitely learned how these reactions proceed individually and which composition is to be viewed as the primary or as the complex bodies resulting from dehydration.

These studies were made in order to develop a furnace for manufacture of K_2MnO_4 at Bitterfeld.

Figure 3 shows four technically operated furnaces. All are gas-fired. They are identified in the drawings by the Greek letter "phi" and by abbreviation "lg", which I assume to be translated into diameter and length, in millimeters. Engineers familiar with abbreviations used by German draftsmen might interpret these dimensions differently.

(1) Flat cast iron pan furnaces of about 2000 "phi" with depth of fill 0.3 meter. Followed by ball mill, then by a second burning in a finishing furnace.

(2) Externally-heated rotary furnace 1800 "phi" and 6000 "lg". Burning is in two stages, with milling between stages.

(3) Internal-flame rotary furnace about 2000 "phi" and about 15000 "lg"

The ore must be milled very fine, about 5-10% residue on 1000-mesh sieve (would this mean 1000 apertures per square centimeter? If correct, this would mean 32 meshes per linear centimeter, [illegible] or 0.16 mm aperture, or about a 90 mesh sieve, U. S. system. Say 5% residue on 80 mesh sieve.

Various tube mills with attached air blowers are used.

In the pan furnace operation the oxidation proceeds slowly and the plant must possess several pans to be used for first and second stages as needed, with ball-milling between stages.

In the externally-heated rotary furnace the reaction is likewise slowed by uncontrolled drying-out and likewise requires milling between initial and final stages of burning. Crusts must periodically be knocked off of the wall of the pre-melt furnace. Overheating cannot be avoided, and the flame is often shut off and then re-lighted.

Based on these observations the I. G. Farbenindustrie plant at Bitterfeld developed a rotary furnace with special features. The finely-milled ore and KOH are introduced in optimum proportions as a dust blown through the flame. The dust is blown through the flame with a blast of hydrogen, and the flame is strongly oxidizing, using air. The moisture content of the air is regulated by adding water. In place of hydrogen, superheated air can be used. The drawings show sketches of the nozzles. The nozzle for use with hydrogen is shown to possess the following, concentric from the center out :

1). Hole for dust of ore, KOH and water.
2). Jacket for compressed air.
3). Jacket for hydrogen.
4). Jacket for air.

The nozzle which uses superheated air introduces the following from the center out :

1). Ore, KOH, and water.
2). Compressed air.
3). Superheated air.

Dimensions of the nozzle are not given; the description is only qualitative showing the order of parts.

At the far end of the rotary the finished melt flows off of the lip of the tube, and the exhaust gases are vented at the top of the lip, that is diametrically above the point where the melt flows off the lip.

This new furnace permits operation in one stage with no intermediate milling and with no troublesome crusting. Yield of 97-98% is enjoyed, based on MnO_2 content. In order not to reduce the capacity of the furnace in the case of very difficulty workable ores, it is preceded by one or two autoclaves in which the ore-KOH mix is given a short pressure-heating at 150-180°C. (Pure KOH melts at 360°C). This hydrates the MnO_2, facilitating subsequent oxidation. The mix is dusted into the rotary furnace directly from the autoclaves. The finished melt is leached with weak water from a previous run, filtered from the gangue, and then converted to $KMnO_4$ by previously described methods.

The solidification by means of CO_2 previously generally used is now not much used because it destroys a third of the manganate, and the resulting potash must be sold or causticized. The use of chlorine avoids this loss of manganate, but consumes an equivalent of alkali.

The oxidation with ozone is very elegant, but is hardly usable because of the high cost of ozone. If used, it works on concentrated liquor and gives pure $KMnO_4$ crystallizing out direct.

There remains the electrolytic oxidation, generally applicable today. Here follows a long page describing and diagramming the equipment and operation of the electrolytic oxidation. Current efficiency 80% with yield 90-98%, working on liquor of strength 130-140 K_2MnO_4 g/l, 0.15 amp/cm^2 and 2.5 volt. This is I. G.'s improvement on other companies, which get current efficiency 60-70% using 0.08000.003 amp per cm^2 and 2.5 to 2.7 volt.

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Also follows two pages describing wet process oxidation of MnO_2 ore or of Mn[illegible]chal or of ferromanganese in alkaline solutions. Also other novelty processes.

F. Craig

8-21-25

F - Literature

Cement Blue, a Product of Barium

This is a cement pigment, but is transparent in oil paints or enamels because it possesses too little opacity. Did not learn refractive index, but it would have to be about that of barium sulfate.

It is a mixed crystal of 10% barium manganate, $BaMnO_4$ in barium sulfate. To make it barium carbonate and barium hydroxide are mixed with potassium manganate, K_2MnO_4, (not the familiar purple potassium permanganate $KMnO_4$) and stirred into dilute sulfuric acid containing nitric acid. A paste forms and is calcined to 600-700°C red heat. It is at this stage that the mixed crystal formation takes place. The calcined product is washed with hydrochloric acid and water to remove the potassium, and filtered, dried, and ground. The tone is sky-blue and the color is very permanent. Cement is its only outlet, for it is no good in paints because of its low index of refraction. (How about roofing grits, made by grinding such cement ?)

Keep in mind that for making such a color for such an application it would probably suffice to use the crude form of potassium manganate intermediate in potassium permanganate manufacture, about which I have a complete translation from the same book, pp. 504 ff, telling how the German I. G. Farbenindustrie makes it at Bitterfeld author E. Müller.

Source of information : Winnacker-Weingaertner, Chemische Technologie, 5 volumes, 1950-1953, published by Carl Hanser Verlag, Munich, in John Crerar Library, Chicago, chapter of Volume "Anorganische II", number on pigments, written by J. Druckor, page 861. Druckor calls attention that this cement blue is one of the three examples of industrially produced mixed crystal pigments the others being molybdate reds, where a small percentage (15%) of lead molybdate (white) causes lead chromate (yellow) to crystallise in a red form, and the cadmium reds, where a small percentage of cadmium selenide causes cadmium sulfide to crystallise red instead of yellow.

F. Craig

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F Lithopone

Lithopone at Leverkusen

Julius Drucker of Leverkusen, Germany, probably of the big [redacted] Farbenfabriken Bayer there, has written the chapter on pigments, both white and colored in the 1950 Winnacker-Weingaertner Chemical Technology, Volume "Anorganische II", pages around 535. Following is a series of notes from his pages on lithopone, avoiding the points which should already be familiar to us as lithopone manufacturers, but noting the old and new details which we may not have developed in our factory.

Refining of Zinc Liquor. There is hardly ever straight sulfate, but is a mixture of sulfate and chloride. They usually oxidize out the iron, manganese, and cobalt first, like we do, but they apply a subsequent oxidation after zinc dusting to remove iron and manganese introduced as impurity in the zinc, which causes them to say that the zinc dusting could be done before the oxidation. In both oxidation and zinc dusting the higher the concentration of liquor, the higher the optimum temperature, over the whole range from 10 to 100°C. Organic material, especially colloidal material, hinders the action of the zinc dust, causing them to simultaneously add active carbon along with zinc dust if such is present. Temperature must be maintained at full heat until filtered, for drop in temperature causes re-solution of precipitated metallic impurities. pH must be correct. Zinc dust activated by a percentage of copper or lead is not superior to straight zinc dust. Fine "pyrogenic" zinc dust is used, and in very large doses, 100 to 1000 times the equivalent of the impurities being removed. Special care is given to removal of nickel, whose sulfide shows in the lithopone most strongly of all impurities, 0.001%, zinc basis, giving objectionable yellow cast to lithopone.

Black Ash Manufacture. High percentage barytes is a thing of the past; they have to live with contaminated grades. Each 1% silica binds 4% barium sulfate inert as fourth barium silicate. They try to avoid using ores containing more than 3% silica. Attempts to bind silica by adding lime or other things, to form calcium silicate, etc., have so far been fruitless. Fluorspar and iron are contamination of barytes is bad because fluorspar they lower the fusion point, cause sintering, and slow down the reduction. The undesirable impurities cause low yields by two mechanisms:

1). By binding barium as barium silicate so that it cannot become barium sulfide, and
2). By slowing down the reduction so that at any practical throughput it does not attain the yield which would otherwise be possible with coarse furnace capacity.

In practice they attain yields of 70 to 90% BaS in the black ash.
Simple filtration of the liquor is all they do toward purification of the barium sulfide, considering that all metals are held by the filter as insoluble sulfides. Aluminum not discussed. They sometimes purposely dissolve in additional sulfur as polysulfide to minimize oxidation in the lithopone calciner. This confirms that polysulfide sulfur precipitates with the zinc the same as monosulfide sulfur.

Lithopone Striking and Finishing. Figures of sulfur are sometimes added to the strike to minimize oxidation in the calciner. When water-glass is added to the strike it makes the finished lithopone soft. Some rotary calciners have the fore-muffle to prevent contact between flame and lithopone; some have the flame right in the calciner like ours. Straight sulfate material is calcined at 650°C, but chloride materials around 450°C. Recent researches show that crude uncalcined lithopone is not a chemical hydrate but only a moisture adsorbate, despite the 400°C heat required to expel last traces of moisture. In calcination only the 20S particles grow; the 80S particles do not. They depend on addition of cobalt salt to minimize light sensitivity of their chloride material, and say that the resulting cobalt sulfide is

taken into the crystal lattice of the zinc sulfide only during the calcining stage, not during the wet stage. Some lithopone is dry-cooled by air (inert gas ? ?) and not quenched if it contains no soluble matter needing to be washed out. Quench water is weakly acid (Verdain says Bayer acidify quench water). Brecher recognizes the futility of milling to reduce [illegible] particle size. They use wet ball mills and Dorr classifiers. Oil absorption for sulfate grades is about 14.5; for chloride grades, about 11. Crude uncalcined lithopone is not light-sensitive.

German Grades of Lithopone. Rotsiegel (Red Seal) is 30% ZnS; Grünsiegel (Green Seal) is 40%; Bronzesiegel (Bronze Seal) is 50%; Silbersiegel (Silver Seal) is 60%. Ö grades (Capital O with umlaut) have added milled barytes supplanting part of the precipitated $BaSO_4$ content, are of low oil absorption, and are used in oil paints wanted to brush easily. Lithonin is a non-settling grade for enamels, treated with fatty acid. WHR-Ware (WHR grade) are hydrophyllic, easily wet with water, for use in water dispersions. "Lithopone-Lackware" (Lithopone Lacquer Grade) has low ZnO content and does not liver in spirit varnish. They list two special grades for weather-resistant use in exterior paints : "Lithoweiss" (Litho White), which is a mixture of lithopone and [illegible] (Zinc Oxide, grade made from metal), evidently not at then in the Farbenfabriken Bayer line, and "Aussenweiss" (Exterior White) which is a mixture of lithopone and BARIUM [illegible] offered by the Sachtleben company.

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