



Chemical synthesis of battery active manganese dioxide
by Earl O Kleinfelder

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
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MANGANESE DIOXIDE

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EARL O. KLEINFELDER

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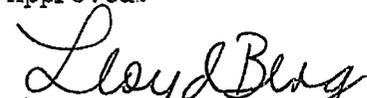
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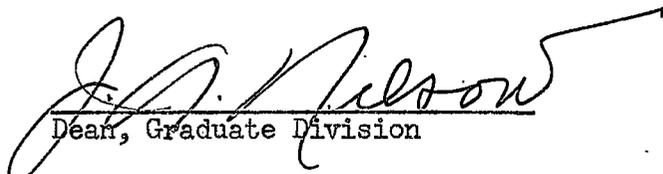
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Montana State College

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LOTION
OLD DANGER BOND
by
FOX RIVER

ABSTRACT

A portion of the third year's work on a project designed to survey chemical syntheses of battery active manganese dioxide is presented here.

Two syntheses that have produced manganese dioxide, which exceeded initial drain specifications, are: the potassium permanganate oxidation of manganous nitrate and the potassium permanganate oxidation of manganous chloride.

The adaptation of domestic ores to commercial production of battery active manganese dioxide by economical chemical syntheses is the ultimate objective of this project.

This report includes a discussion of the sample preparations and performance of the manganese dioxide samples from three syntheses using chemically pure reagents. Also reported are the chemical analyses of the samples, consisting of values for total manganese, available oxygen, moisture content, and pH. Apparent densities, bobbin weights, and initial drain test performances are tabulated with the chemical analyses.

INTRODUCTION

Manganese dioxide, the depolarizing component in the Leclanche type dry cell, is of particular interest to the United States Army Signal Corps since they are a major consumer of dry cells.

At present, the two sources of battery active manganese dioxide are natural African Gold Coast ore and electrolytic material. Several disadvantages in the use of Gold Coast ore are its limited depolarizing power and the long shipping distance involved from Africa to the United States. While electrolytic manganese dioxide has greater depolarizing power than Gold Coast ore, its cost is high due to the complexity of its manufacture. The United States Army Signal Corps, therefore, initiated a research project to investigate the feasibility of producing specification grade manganese dioxide by chemical processes. The ultimate goal of this project is the development of a commercially feasible chemical process which uses United States ore as a source of manganese.

Previous work at Montana State College on this project has been reported in theses by Nickelson (1), Davidson (2), Moore (3), Fahlgren (4), and Sadagopachari (5).

The purpose of this investigation was to determine if specification grade battery active manganese dioxide could be produced from several chemical syntheses involving potassium permanganate. These syntheses are: the oxidation of manganous nitrate by potassium permanganate, the oxidation of manganous chloride by potassium permanganate, and the oxidation of manganous sulfate by potassium permanganate. A series of investigations was then carried out on the more promising syntheses to determine the

optimum reaction conditions necessary to produce material that would meet or exceed drain specifications.

The depolarizing power of a given sample of manganese dioxide was determined by making size "A" batteries in which the only variable of composition was the manganese dioxide, and then subjecting these batteries to standard drain tests. The number of hours of battery life, as evaluated by the drain tests, determined the depolarizing power of the manganese dioxide. It should be pointed out that the terms: depolarizing power, battery activity, and drain life are synonymous.

SPECIFICATIONS

The following specifications have been tentatively established by the Signal Corps as of March 18, 1952, for acceptable synthetic manganese dioxide depolarizers. These specifications are taken from Bulletin SCL-3117-D (6).

Chemical Composition

Available oxygen as MnO ₂	85.0 % min.
Total manganese as Mn	58.0 % min.
Absorbed moisture as H ₂ O	3.0 % max.
Iron as Fe (soluble in HCl)	0.3 % max.
Silicon as SiO ₂	0.5 % max.
Total alkali and alkaline earth metals	1.0 % max.
Total heavy metals (other than Fe, Pb)	0.3 % max.
Lead as Pb	0.2 % max.
pH	4.0-8.0

Apparent Density

The synthetic manganese dioxide shall have an apparent density between 20-30 grams per cubic inch.

Particle Size

The synthetic manganese dioxide shall be of such size that at least 65 percent of the material shall pass through a U. S. Standard Sieve No. 200 and at least 90 percent through a U. S. Standard Sieve No. 100.

Crystalline Phase

From crystallographic and microstructural analyses, predominance of the imperfectly crystallized phase known as gamma manganese dioxide should be evident.

Particle Morphology

The particle shall present irregular shapes with no evidence of cleavage (that is, with non-rectilinear profiles having nebulous rather than sharp, well-defined edges) when examined at direct magnification from 5,000 to 20,000 diameters.

X-Ray Diffraction Pattern

The X-Ray diffraction pattern shall be characterized by the diffuse line pattern of gamma manganese dioxide. Significant lines, d , of gamma manganese and their respective relative intensities, I , for iron radiation are as follows:

<u>d</u>	<u>I</u>
4.00	5
2.45	7
2.14	7
1.65	10
1.40	5
1.06	3

Figure 3, in the Appendix, shows the various diffraction patterns of the seven types of manganese dioxide.

Battery Life

The specifications for discharge of standard "A" size cells are as follows:

	<u>Low-Drain</u>	<u>High-Drain</u>
Type of discharge	continuous	continuous
Discharge resistance	166.67 ohms	16.67 ohms
End voltage	1.13 volts	1.00 volts
Temperature	70°F	70°F
Relative humidity	50%	50%
Battery life	130 hours (min.)	5.5 hours (min.)

MATERIALS AND METHODS

Reagents

Although the goal of this project is to develop chemical syntheses for producing battery active manganese dioxide from commercially available ores, only reagent grade chemicals have been used in this study. The immediate problem was to produce specification grade product, leaving purity difficulties inherent in work with ores to be overcome during a later phase of the project. Data obtained in this study with pure reagents will be used as a guide in selecting processes suitable for study in adaptations of commercial ores.

Syntheses

Methods of preparations of samples discussed in this thesis are shown in Table II of the Appendix. The steps for preparation of a sample are as follows:

1. Make solutions of reactants of a desired concentration.
2. Heat the manganous salt solution to the desired reaction temperature in 10 or 20 liter Pyrex vessels.

3. Add the KMnO_4 solution in a dropwise manner, at a uniform rate, to the hot manganous salt for a desired length of time.
4. Maintain the reaction mixture at the reaction temperature for a desired length of time.
5. Allow the reaction mixture to cool, with agitation, for approximately 24 hours.
6. Wash the product by adding hot tap H_2O , agitate the mixture for 20 to 30 minutes, allow the product to settle, and decant the supernatant liquid; this procedure is continued until the pH of the supernatant liquid reaches 6.5-7.0.
7. Filter the product on a fritted glass filter and remove the cake to an evaporating dish.
8. Dry the product in an electric oven at a temperature of between 105° to 110°C for approximately 24 hours.
9. Weigh sample and place in an airtight bottle for storage.
10. Ball-mill sample for a desired length of time in a 3.5 gallon size pebble mill revolving at 60 rpm and charged with approximately 5.5 lb of flint pebbles of about one-inch diameter.
11. Screen the product through a U. S. Standard Sieve No. 40, the ≈ 40 mesh portion is retained and stored for testing.
12. Carry out various analytical tests on the sample (see Table I of the Appendix.)
13. Fabricate from 6 to 10 "A" cells for testing.

Notes for steps 1-6: the reaction mixture is under constant agitation from stirrers powered by small variable speed motors; the reaction volume is maintained constant usually by additions of small amounts of hot H_2O ; temperature is controlled by use of the multiple switches of a 220 volt electric hot plate; in some cases (see Table II of the Appendix) the order of several of these steps may be interchanged or the steps modified.

The main variables encountered in this investigation are: temperature of reaction, concentration of reactants, time of reaction, and time of

ball-milling. These variables, for a particular synthesis, are correlated with battery life, and these correlations are noted in the discussion section. The wide scope of this investigation and time limitations have prevented the making of complete studies of reaction variables. Studies that have been made were on batchwise reactions, leaving continuous processing for future investigation.

Battery Fabrication and Testing

From 6 to 10 standard "A" size dry cells were constructed in accordance with usual cell assembly techniques. Signal Corps specifications were followed in proportioning the various mixtures and solutions that were used. A mixture containing 80 percent by weight of the MnO_2 sample, 8 percent Shawinigan carbon black, and 12 percent NH_4Cl were mixed in a one-quart size pebble mill for 20 minutes to assure uniform consistency. This mixture was dampened with a wetting solution consisting of 5.8 percent NH_4Cl by weight, 8.6 percent $ZnCl_2$, and 85.6 percent H_2O until material acceptable for tamping was obtained.

From the mixture described above, bobbins were tamped in an apparatus as shown by Figure 1 of the Appendix. Due to the corrosiveness of the mixture used in bobbin making, Stellite and methacrylate plastic were utilized for the parts of the apparatus which would contact the mixture. Use of the Stellite die also was advantageous, since it produced smooth-sided bobbins.

Still in accordance with Signal Corps specifications, the bobbins were wrapped in cotton gauze, tied with cotton thread, and set in zinc cans with a cold paste electrolyte containing a ratio of 50 ml of a solution consist-

ing of 23.7 percent NH_4Cl by weight, 22.3 percent ZnCl_2 , 0.1 percent HgCl_2 , and 53.9 percent H_2O to 10.7 gm of a mixture containing 74.7 percent corn-starch and 25.3 percent flour. A paper washer was placed around the carbon rod, a brass cap was pressed on the rod, and then the bobbin was sealed in the can with hot sealing wax.

After a period of 7 to 10 days, the cells were screened for open voltage and then from 4 to 6 cells were discharged through test resistances as partially diagrammed in Figure 2 of the Appendix. The test rack consisted of eight 16.67 ohm resistances, twenty-four 166.7 ohm resistances, and an open voltage circuit through the voltmeter. The test rack was placed in an insulated box where the temperature was controlled at $70 \pm 2^\circ\text{F}$. The insulated box also served as a storage place for all untested cells. End voltages for the drain tests were 1.13 volts for the 166.7 ohm drain, called low drain (L.D.); and 1.00 volts for the 16.67 ohm drain, called high drain (H.D.).

The permanent voltmeter in the test rack consisted of a Simpson 50 microampere ammeter in series with a 330,000 ohm carbon resistor and a 10,000 ohm variable resistor. This instrument was calibrated with a standard voltmeter before any drain tests were conducted. It was found that true voltage values from 1.00 to 1.20 volts could be read directly from the meter's scale. The meter could be read to an accuracy of ± 0.005 volts. The calibration of the voltmeter was tested periodically by measuring the voltage of a standard cell on the open voltage circuit. It was found in all cases that the calibration of the voltmeter had remained constant. This voltmeter had the inherent advantage of drawing only a

small amount of current from the test cell whenever a voltage reading was made.

After a period of three months, from one to three cells of a particular sample were tested for low drain life. The three-months drain life of the cells is an indication of the sample's shelf-life. The U. S. Army Signal Corps specification for the three-months drain life is that the cells on the three-months test will give 85 percent or greater of the initial drain life.

Oxygen Analysis

Available oxygen determinations were made in accordance with Signal Corps methods as stated in Bulletin SCL-3117-D (6). The determination was made as follows:

A sample of dried ore (approximately 0.2 gm) was weighed accurately into a 400 ml beaker fitted with a close fitting watch glass. Exactly 50 ml of a stock solution of ferrous ammonium sulfate of known concentration (approximately 0.2 N) were added from a pipette. In a similar beaker there was placed exactly 50 ml of the ferrous ammonium sulfate stock solution to serve as a control. Both the original sample and the control sample were diluted to 150 ml with distilled water and digested on a steam bath with occasional stirring until solution of the ore was effected. The solutions were allowed to cool and the volumes were adjusted to about 200 ml. The samples were then titrated with a solution of potassium dichromate of known concentration (approximately 0.2 N) using a potentiometric method.

Total Manganese Analysis

A sample of dried ore (approximately 0.1 gm) was weighed accurately

into a 500 cc conical flask. Ten ml of distilled water and five ml of concentrated hydrochloric acid were added and the sample was dissolved by heating. The solution was evaporated almost to dryness and cooled. Twenty-five ml of concentrated sulfuric acid and ten ml of concentrated nitric acid were added and the solution was heated strongly until there was no further evolution of brown fumes.

After cooling, 275-300 ml water and three gms of sodium bismuthate were added. The mixture was stirred for five minutes and filtered, with suction, through a fine fritted glass funnel into a 500 ml side arm flask. The funnel containing excess bismuthate was washed several times with distilled water to remove traces of permanganic acid. The filtrate and washings were transferred quantitatively into a 1000 ml beaker containing 50 ml of hot oxalate solution and 100 ml of 10% sulfuric acid. This was heated almost to boiling and the excess oxalate was titrated with 0.1 N potassium permanganate.

pH Determination

A sample of dried ore (approximately one gm) was accurately weighed into a 250 ml Erlenmeyer flask and exactly 100 times the weight of distilled water was added. The outside wall of the flask was then marked at this level. The contents of the flask were boiled actively for fifteen minutes, the water lost by evaporation was replaced, and the mixture was again brought to boiling. The flask was fitted with tubes containing ascarite and cooled to room temperature. The contents were transferred to a suitable beaker and the pH was then determined on the slurry by means of a Beckman pH meter after stirring the mixture to obtain a uniform suspension.

Apparent Density

Apparent density was determined by running the -40 mesh portion of the ball-milled sample through a Scott volumeter into a cubic inch container. The apparent density was reported as grams per cubic inch.

Moisture Content

A sample weighing two to three grams was dried for 16 hours at a temperature of 105-110°C. The loss in weight was taken as the free moisture content.

X-Ray and Spectrochemical Analyses

X-Ray and spectrochemical analyses of the samples were done at the Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey. The methods used, as described by them, are as follows:

X-Ray diffraction: X-Ray diffraction powder patterns of portions of the samples were prepared using iron K alpha radiation in a Debye-type camera yielding a dispersion of one degree of two theta per millimeter of film.

Spectrochemical analysis: The sample was burned to completion in a D.C. arc and the resultant spectra photographed. A specially selected spectrum line of each of the various constituent elements was measured for intensity and compared with the intensity of the manganese internal standard line. These data were used to determine the percentages of the elements present, using previously established working curves. The amounts of sodium and potassium were determined by a modified method whereby lithium was the internal standard line instead of the manganese line.

DISCUSSION OF RESULTS

Three syntheses were investigated in this study. The overall process was the reaction of a soluble manganous salt with potassium permanganate to give a product of mainly hydrated manganese dioxide. Several series of reactions were carried out to determine the effects of: reaction concentration, reaction temperature, reaction time, and ball-milling time on drain life. A few reactions were carried out to shed light on the mechanism of the syntheses.

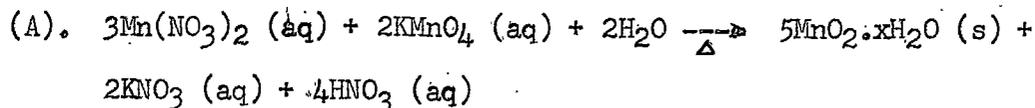
Reactions were formulated in the most probable manner as indicated by experimental observations and literature references such as Bolen and Weil (7) and Mellor (8). Methods of preparations and analytical and test data for the manganese dioxide samples produced in this study are shown in Table I and Table II of the Appendix.

A code was used to designate the different samples. The first portion of the code indicates the source of manganese; i.e. K for manganous chloride, N for manganous nitrate, and S for manganous sulfate. The second portion of the code indicates the oxidizing agent; in all reactions potassium permanganate was used and coded KP. The third portion of the code indicates the sample number. In some reactions, where the sample was divided into two or more portions, each portion was also coded with a small letter. An example of this code would be reaction N-KP-2a, where N stands for manganous nitrate, KP stands for potassium permanganate, and 2a stands for the first portion of sample 2.

The Potassium Permanganate Oxidation of Manganous Nitrate

This study was termed the N-KP synthesis. The general overall

chemical equation is:



This equation was found to be stoichiometrically correct if the potassium permanganate solution was added to the hot manganous nitrate solution. When the reaction was carried out in the above manner, the final product (manganese dioxide) contained 95.5 percent of the manganese initially present in the reaction mixture. In reaction N-KP-15, the manganous nitrate solution was added to the hot potassium permanganate solution and only 60 percent of the initial manganese content was recovered in the final product. In view of the low yield, it seemed that equation (A) was no longer completely true for this reaction. The above figures for the percent recovery of product as manganese did not take into account small losses of the product during the washing operation.

From the analytical data, it was found that the final product contained mainly MnO_2 and small amounts of MnO and H_2O . These three components were probably bound together to form relatively stable compounds. Several references in Mellor (8) stated that compounds such as $16\text{MnO}_2 \cdot x\text{H}_2\text{O}$ had been found in the product from reaction (A).

A manganese dioxide, giving 6.0 hrs high-drain life and 146 hrs low-drain life, was produced when 1.33 mols HNO_3 were added to the manganous nitrate solution of reaction N-KP-21. This reaction was carried out in the same manner as reaction N-KP-9 except that no HNO_3 was added to reaction N-KP-9. The manganese dioxide from reaction N-KP-9 gave only 3.6 hrs high-drain life and 136 hrs low-drain life. From this comparison, it was found

that the addition of HNO_3 to the initial reaction mixture produced a manganese dioxide of superior drain life.

Reaction Concentration Study

A series of seven reactions (N-KP-3, -4a, -5, -6, -12a, and -14a) was carried out to determine the effect of reaction concentration on drain life. Reaction concentration was defined as the initial gm-mols of manganese nitrate present in a reaction divided by the total reaction volume in liters. In this series of seven reactions, the other variables; i.e. reaction time, reaction temperature, and time of ball-milling, were held essentially constant.

It was found that the high-drain life of cells made from the material of these seven reactions increased from 0.5 hours to 5.8 hours as the reaction concentration was increased from 0.0625 mols per liter to 1.0 mols per liter. This is shown in Figure 4. The same tendency was noted in the low-drain life of the cells; i.e. the low-drain life of the cells increased from 45 hours to 136 hours as the reaction concentration was increased from 0.0625 mols per liter to 1.0 mols per liter. This is shown in Figure 5. The manganese dioxide from reaction N-KP-5 gave a low-drain life of 160 hours, but a duplicate of this reaction, N-KP-12a, gave only a low-drain life of 123 hours. A possible explanation for this discrepancy is that approximately ten percent of the product from reaction N-KP-5 was washed away as a brown colloidal suspension, but no such effect was noted when the product from reaction N-KP-12a was washed. Disregarding reaction N-KP-5, the best drain life resulted from reaction N-KP-7a which gave 5.8 hours high-drain life and 136 hours low-drain life. This manganese di-

oxide exceeded the drain specifications of the U. S. Army Signal Corps (6). In general, it may be concluded from this study that drain life increased as the reaction concentration was increased. Although this study did not show the optimum reaction concentration, it may be possible to produce a manganese dioxide which exceeds 5.8 hours high-drain and 136 hours low-drain when using a reaction concentration approaching the saturation concentration of manganous nitrate.

Reaction Temperature Study

A series of five reactions (N-KP-5, -8a, -10, -11, and -12a) was carried out to determine the effect of reaction temperature on drain life. In this series of reactions the other three variables were held essentially constant. It was found that both the high-drain life and the low-drain life increased from 1.3 hours to 5.1 hours and from 40 hours to 138 hours, respectively, as the reaction temperature was increased from 65°C to 92.5°C. This is shown in Figure 6 and Figure 7. Drain data for the manganese dioxide from reaction N-KP-5 was disregarded in light of the information given in the preceding paragraph. This study was carried out at a reaction concentration of 0.25 mols per liter and so in light of the results from the reaction concentration study, it may be expected that drain lives greater than 5.1 hours high drain and 138 hours low drain, would result from manganese dioxide produced at higher reaction concentrations. This was shown by the comparison of reaction N-KP-12a with reaction N-KP-18b.

Reaction	Reaction Temperature	Reaction Concentration	High-Drain Life, Hrs	Low-Drain Life, Hrs
N-KP-12a	85°C	0.25	4.5	123
N-KP-18b	85°C	1.00	5.5	148

It is possible that reactions carried out under pressure and reaction temperatures approaching 200°C will produce manganese dioxide that will exceed drain specifications.

Reaction Time Study

A series of five reactions was carried out to determine the effect of reaction time on drain life. See Table III of the Appendix for pertinent data. The time of reaction was defined as the sum of (1) the time of adding the potassium permanganate solution to the manganous nitrate solution; (2) the digestion period, defined as the time that the reaction mixture was held at the reaction temperature in excess of time (1); and (3) the time of cooling before the product was washed.

By comparing reaction N-KP-9 with reaction N-KP-19, reaction N-KP-9 with reaction N-KP-20, and reaction N-KP-9 with reaction N-KP-6; it was noted that when the time of adding the potassium permanganate solution, the digestion period, and the time of cooling, respectively, was increased, the drain life increased. Poor drain life characterized the material produced by reaction N-KP-17, where a hot potassium permanganate solution was added quickly to the hot manganous nitrate solution.

This study revealed that both a four-hour period for the time of adding the potassium permanganate solution to the reaction mixture, and a four-hour digestion period were necessary to produce manganese dioxide that met both high-drain and low-drain specifications. It is possible that longer reaction periods would produce a material that would give a superior drain life.

Time of Ball-Milling Study

A series of seven reactions was carried out to determine the optimum ball-milling time for the dried reaction product. See Table IV for pertinent data. Previous work by Moore (3), Fahlgren (4), and Sadagopachari (5) revealed that, in general, a ball-milling period of two hours produced manganese dioxide of higher drain life.

Six of the reactions were designed so that two portions could be ball-milled for two hours and four hours, respectively. As shown by the data in Table III, an increase in ball-milling time from two hours to four hours had either very little beneficial effect or a detrimental effect on both high-drain life and low-drain life of cells produced from material that either met or nearly met drain specifications. In general it was found that as the reaction concentration was increased, an increase in ball-milling time of from two hours to four hours for the reaction product reduced both high-drain life and low-drain life of the manganese dioxide.

Reaction N-KP-18 was designed so that five samples could be ball-milled for different lengths of time. As shown in Figure 8, a ball-milling period of one hour produced the greatest high-drain life (5.5 hrs). The high-drain life decreased slightly as the ball-milling periods were increased.

The effect of ball-milling time on low-drain life is shown in Figure 9. It was found that a ball-milling period of one hour produced a material which gave 148 hours low-drain life. Longer periods of ball-milling (up to 8 hrs) produced material of essentially the same low-drain life.

Reaction N-KP-18 was carried out at or near those reaction conditions

where maximum drain life occurred, as indicated by the various studies of reaction variables.

From this study it may be concluded that a ball-milling period of from one to two hours will increase the drain life of manganese dioxide which is produced at the more favorable reaction conditions of concentration, temperature, and time. Ball-milling periods longer than two hours (up to eight hours) for this manganese dioxide produced material of essentially the same drain life.

It is expected that the drain life of manganese dioxide produced at optimum reaction conditions and ball-milled for a period of from one to two hours will exceed the 5.5 hours high-drain life and the 148 hours low-drain life of reaction N-KP-18b.

Three-Months Drain Tests

As shown in Table I, only five three-months drain tests are yet available. The three samples that had low-drain lives, which exceeded low-drain specifications, gave three-months drain lives of from 75 percent to 85 percent of the initial low-drain life. Further three-months drain tests will give a better indication of the shelf-life of the manganese dioxide produced by the N-KP synthesis.

Physical and Chemical Properties of the Product

All the N-KP reactions that produced manganese dioxide, which met or exceeded one or both of the drain specifications, also met the U. S. Army Signal Corps specifications (6) for percent O_2 as MnO_2 , percent Mn, percent H_2O , pH, and bobbin weight. Although none of these reactions produced manganese dioxide which met the specifications for apparent density of

from 20 gms per cubic-inch to 30 gms per cubic-inch, this manganese dioxide gave drain lives which exceeded specifications. The manganese dioxide, meeting drain specifications, had an apparent density of from 13 gms per cubic-inch to 15.5 gms per cubic-inch. It is believed that the specification for the apparent density of chemical manganese dioxide should be changed to 10 gms per cubic-inch or over. This is in accord with the recommendation made by Sadagopachari (5).

Future Work Concerning the N-KP Synthesis

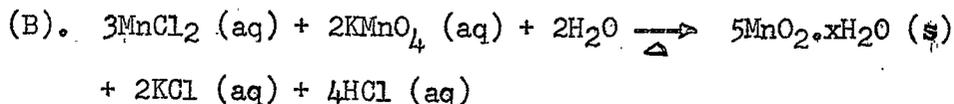
The various studies of the variables of the N-KP synthesis indicate that the following reactions should be carried out:

1. One or more reactions where the following conditions are incorporated: a reaction concentration of 1.0 mols per liter, a reaction temperature of 93°C, a reaction time of eight hours which includes a four-hour period to add the potassium permanganate solution and a four-hour digestion period, and a two-hour ball-milling period.
2. A series of reactions where the following conditions are incorporated: reaction concentrations from 1.0 mols per liter to the saturation concentration of the manganous nitrate solution, reaction temperatures of from 93°C to 200°C, a reaction period of longer than eight hours which includes a period longer than four hours to add the potassium permanganate solution and a digestion period longer than four hours, and a ball-milling period of from one to two hours.
3. A series of reactions where various amounts of HNO₃ are added to

the manganous nitrate solution.

The Potassium Permanganate Oxidation of Manganous Chloride

This study was termed the K-KP synthesis. The general overall chemical equation is:



This equation was found to be stoichiometrically correct when the potassium permanganate solution was added to the hot manganous chloride solution. The yields, on a manganese basis, of the K-KP reactions were found to be 95⁺5 percent. The yields of several reactions, listed in Table I, were not reported because an excessive mechanical loss of product occurred during the washing operation.

The analytical data in Table I, show that the product from the K-KP synthesis are very similar to the product from the N-KP synthesis.

Reaction Concentration Study

A series of five reactions (K-KP-1, -2, -3, -4a, and -5a) was carried out to determine the effect of reaction concentration on drain life. As shown in Table II, the other variables; i.e., reaction temperature, reaction time, and ball-milling time were held essentially constant.

It was found that the high-drain life increased from 3.3 hours to 5.0 hours then decreased to 3.3 hours as the reaction concentration was increased from 0.0625 mols per liter to 1.0 mols per liter. As shown in Figure 10, the maximum high-drain life occurred at a reaction concentration of 0.25 mols per liter. Figure 11, reveals that the low-drain life increased from 93 hours to 132 hours as the reaction concentration was

increased from 0.0625 mols per liter to 1.0 mols per liter.

This study has shown that manganese dioxide, which nearly met drain specifications, can be produced at reaction concentrations of from 0.25 mols per liter to approximately 0.40 mols per liter.

Reaction Temperature Study

A series of four reactions (K-KP-2, -6a, -8, and -10) was carried out to determine the effect of reaction temperature on drain life. In this study the other three variables were held essentially constant. A reaction concentration of 0.25 mols per liter was used for the reactions in this study.

As shown in Figure 12, the high-drain life increased from 3.1 hours to 5.0 hours then decreased to 0.3 hours as the reaction temperature was increased from 65°C to 93°C. The maximum high-drain life occurred at a reaction temperature of 85°C. Figure 13 reveals that the low-drain life increased from 144 hours to 154 hours then decreased to 16 hours as the reaction temperature was increased from 65°C to 93°C. The maximum low-drain life occurred at a reaction temperature of 75°C.

This study has shown that manganese dioxide, exceeding low-drain specifications, could be produced at reaction temperatures of from 65°C to approximately 83°C, but that the manganese dioxide, produced in this temperature range, would not meet the high-drain specification. It is probable that manganese dioxide, meeting both drain specifications, can be produced at a reaction temperature of 80°C and at near optimum conditions of reaction concentration and reaction time.

Reaction Time Study

A series of four reactions was carried out to determine the effect of reaction time on drain life. See Table V for pertinent data. Reaction time was defined the same as in the N-KP synthesis.

By comparing the manganese dioxide from reaction K-KP-7 with the manganese dioxide from reaction K-KP-3, it was found that the high-drain life decreased from 5.5 hours to 2.2 hours and the low-drain life remained constant at 130 hours as the cooling time was increased from 0 hours to 18 hours. The time of adding the potassium permanganate solution and the digestion period were the same for these two reactions. It may be concluded that a cooling period is detrimental to high-drain life but has little effect on low-drain life.

By comparing the manganese dioxide from reaction K-KP-11 with the manganese dioxide from reaction K-KP-7, it was found that the high-drain life increased from 4.6 hours to 5.5 hours and the low-drain life decreased from 152 hours to 130 hours as the digestion period was increased from 2 hours to 3.5 hours. The time of adding the potassium permanganate and the cooling period were essentially the same for the two reactions. It may be concluded that an increase in the digestion period increases the high-drain life but decreases the low-drain life.

By comparing the manganese dioxide from reaction K-KP-7 with the manganese dioxide from reaction K-KP-12, it was found that the high-drain life decreased from 5.5 hours to 3.0 hours and the low-drain life increased from 130 hours to 144 hours as the time of adding the potassium permanganate solution was increased from 2.5 hours to 4 hours. The two reactions

had essentially equal digestion periods and equal cooling periods. Although these two reactions were carried out at different reaction concentrations, the effects, described above, on drain life cannot be explained by the results learned from the reaction concentration study. In general it may be concluded that an increase in the time of adding the potassium permanganate solution will decrease the high-drain life and increase the low-drain life.

As indicated by this study, the following reaction time is proposed: a period of 2.5 hours or less to add the potassium permanganate solution, a digestion period of from 2 hours to 3.5 hours, and no cooling period. It is expected that manganese dioxide produced from a reaction using this proposed reaction time will exceed drain specifications.

Time of Ball-Milling Study

Reaction K-KP-18 was carried out to determine the effect of ball-milling on drain life for manganese dioxide which was produced at near optimum conditions of reaction concentration and reaction temperature (see Table II for data pertaining to the reaction conditions). In light of the conclusions from the time of reaction study, the reaction time of reaction K-KP-18 was too long.

As shown in Figure 14 and Figure 15, the maximum high-drain life of 5.1 hours and the maximum low-drain life of 154 hours occurred when the reaction product was ball-milled for a period of 5 hours. A ball-milling period longer than five hours (up to eight hours) seems to cause little change in the drain life. This manganese dioxide exceeded the low-drain specification but failed to meet the high-drain specification.

It is probable that manganese dioxide, meeting both drain specifications, can be produced by a reaction which is carried out at optimum reaction conditions. The proposed time of ball-milling for this manganese dioxide is five hours.

Three-Months Drain Tests

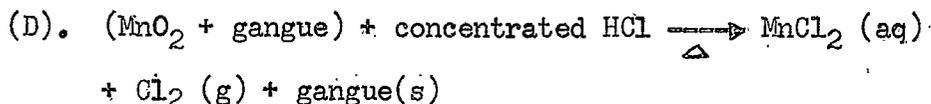
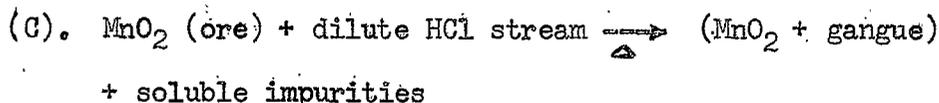
As shown in Table I, only four three-months drain tests are yet available. The manganese dioxide from reactions K-KP-4a and K-KP-4b, which had initial low-drain lives that nearly met the low-drain specifications, gave three-months drain lives of 69 percent and 98 percent, respectively, of the initial drain life. Further three-months drain tests will give a better indication of the shelf-life of the manganese dioxide produced by the K-KP synthesis.

Partial Cost Analysis for the K-KP Synthesis

This cost analysis of the K-KP synthesis covers a cost estimate for the reactants necessary for the synthesis. The overall chemical reaction is:

$$(B). \quad 3\text{MnCl}_2 (\text{aq}) + 2\text{KMnO}_4 (\text{aq}) + 2\text{H}_2\text{O} \xrightarrow{\Delta} 5\text{MnO}_2 \cdot x\text{H}_2\text{O} (\text{s}) \\ + \frac{2\text{KCl} (\text{aq}) + 4\text{HCl} (\text{aq})}{\text{dilute HCl stream}}$$

The proposed method of ore treatment is:



Reaction (B) will be carried out at the conditions suggested from the K-KP synthesis study. The battery active manganese dioxide from reaction

(B) is easily filtered from the reaction mixture and then the hot filtrate (the dilute HCl stream) is used for the initial leach of the finely ground ore as shown in reaction (C). (Note - it will probably not be economical to recover the KCl from the filtrate of (B) since the market price for 99.9 percent pure KCl is only about one cent per pound). The dilute HCl in reaction (C) will react with the carbonates and the more reactive oxides present in the ore but not with the MnO_2 and gangue. The partially leached ore from reaction (C) is filtered (the filtrate will contain much of the impurities initially present in the ore) and then it is further leached with commercial HCl of approximately 22° Be. as shown in reaction (D) to yield the manganous chloride solution needed for reaction (B). The success of this proposed method of ore treatment depends mainly on the manganese being present in the ore as MnO_2 rather than Mn_2O_3 or Mn_3O_4 since some manganese from the higher oxides would be lost in the filtrate from reaction (C). The reaction of the higher oxides with dilute HCl is as follows:



It should be pointed out that the ore treatment process outlined in reactions (C) and (D) is proposed only in a tentative manner since one of several other ore treatment processes may prove to be more economical. These processes could recover the manganese either as manganous chloride or manganous nitrate since reactions (B) and (C) will work as well with $Mn(NO_3)_2$ and HNO_3 respectively.

Philippine ore is used for the partial cost analysis, given below,

because the manganese is present mainly as MnO_2 and its unit cost of manganese is the lowest of the commercially available ores. The costs for reactants in reaction (B), (C), and (D) are as follows:

Reactant	Pounds of reactant per 100 pounds of battery active MnO_2	Cost per* Pound \$	Total \$
$KMnO_4$	72.5	0.225	16.33
Ore**	38 (lbs Mn)	0.0605***	2.24
HCl (22°Be)	100.4	0.05	<u>5.02</u>
			\$23.59

*These prices are taken from the March 29, 1954 issue of Chemical and Engineering News.

**This is Philippine ore and the price is f.o.b. New York.

***This cost assumes a 90 percent recovery of manganese from the ore.

If a 95 percent efficiency is assumed in reactions (B), (C), and (D) then the total cost for reactants becomes \$24.80 per 100 pounds of battery active manganese dioxide or 24.8 cents per pound.

Although no estimate is made for costs other than reactants, the cost of reactants (as estimated above) together with the other process costs will probably make the manganese dioxide produced by this synthesis non-competitive with electrolytic manganese dioxide which sells for 35 to 40 cents per pound. Since the cost of potassium permanganate is 70 percent of the total cost for reactants, some source of potassium permanganate other than commercial crystals, would probably reduce the total process cost considerably. The final solution, in the commercial potassium permanganate process, would probably prove to be an excellent source of

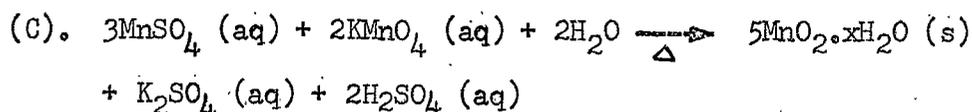
potassium permanganate for use in reaction (B). By use of such a source of potassium permanganate, the total process cost would probably be reduced to a point where the selling price of the manganese dioxide produced by the K-KP synthesis would be competitive with electrolytic manganese dioxide.

Future Work Concerning the K-KP Synthesis

The various studies on the variables of the K-KP synthesis indicate that several reactions should be carried out which incorporate the following conditions: reaction concentration of from 0.25 mols per liter to 0.40 mols per liter, a reaction temperature of 80°C, reaction time of from 4 to 6 hours, and a ball-milling period of 5 hours.

The Potassium Permanganate Oxidation of Manganous Sulfate

This study was termed the S-KP synthesis. The general overall chemical equation is:



The reactions of this synthesis, listed in Table I and Table II, were carried out in a manner similar to the reactions of the N-KP and the K-KP syntheses as described in the section, "Materials and Methods." As shown in Table I, the manganese dioxide from the S-KP reactions exhibited comparable analytical data to the manganese dioxide of the N-KP and K-KP reactions, but had poor drain life.

The reaction concentration study has shown that specification grade manganese dioxide could not be produced from the five S-KP reactions at concentrations of from 0.0625 to 1.0 mols of MnSO_4 per liters of reaction

volume. Although complete studies were not made on all the reaction variables, the poor drain life of the manganese dioxide from five reactions revealed that it was unlikely that specification grade manganese dioxide could be produced from this synthesis.

SUMMARY

The N-KP Synthesis

The study of the N-KP synthesis has shown that manganese dioxide, exceeding both high-drain and low-drain specifications of the U. S. Army Signal Corps (6), can be produced by this synthesis. This manganese dioxide also met the specifications for percent O_2 as MnO_2 , percent Mn, percent H_2O , pH, and bobbin weight,

It is believed that the specification for the apparent density of chemical manganese dioxide should be changed to 10 gms per cubic-inch or over.

The proposed conditions for the N-KP synthesis are as follows: a reaction concentration of 1.0 mols per liter, a reaction temperature of $93^{\circ}C$, a reaction time of 8 hours, and a ball-milling period of 2 hours. Future work will determine if manganese dioxide of superior drain life can be produced: when the reactions are carried out at the proposed conditions, when the variables of the proposed conditions are increased in magnitude, and when HNO_3 is added to the manganous nitrate solution.

The K-KP Synthesis

The study of the K-KP synthesis has shown that manganese dioxide, meeting the high-drain specification and exceeding the low-drain specification, can be produced by this synthesis. The chemical and physical

properties of the manganese dioxide produced by the K-KP synthesis were very similar to those of the manganese dioxide produced by the N-KP synthesis.

The proposed conditions for the K-KP synthesis are as follows: a reaction concentration of 0.30 mols per liter, a reaction temperature of 80°C, a reaction time of 4 hours, and a ball-milling time of 5 hours. Future work will determine if manganese dioxide of superior drain life can be produced when the reaction is carried out in the proposed manner.

The S-KP Synthesis

None of the reactions of the S-KP synthesis produced a manganese dioxide which met drain specifications. From the results of this investigation, it is doubtful that manganese dioxide, meeting drain specifications, can be produced from this synthesis.

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