



Chemical synthesis of battery active manganese dioxide  
by William E Domning

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering  
Montana State University  
© Copyright by William E Domning (1955)

**Abstract:**

A study of the battery activity of the manganese dioxide produced by the oxidation of manganese sulfate by potassium permanganate is presented.

It was the purpose of this work to produce a manganese dioxide from this reaction that would meet drain specifications and to investigate the commercial possibilities of the reaction. A discussion of the sample preparation and performance of the manganese dioxide produced by this synthesis is given. Chemical analyses, which includes total manganese, available oxygen, moisture content, and pH, are tabulated for each manganese dioxide sample as are apparent density, bobbin weight and initial drain test performance. A cost analysis of a proposed ten ton per day plant to produce manganese dioxide by the above synthesis is included.

Heat treating of the manganese dioxide made by the above reaction will produce a manganese dioxide that will meet low drain specifications. A suggested method of preparation of a sample by the above procedure is; purification of a technical grade manganese sulfate by the addition of 10 grams of zinc oxide per 124 grams of manganese sulfate, adjustment of the volume of the manganese sulfate solution until the concentration is 88.6 grams per liter, addition, at the rate of 26.25 grams per hour per 124 grams manganese sulfate, of potassium permanganate of a concentration of 52.5 grams per liter. The reaction is to be run at the boiling point. After, washing, filtering and drying the product, it is to be heated for 6 hours at 220 degrees centigrade.

Material meeting both high drain and low drain specifications was produced from technical grade manganese sulfate and potassium permanganate. The conditions of a successful reaction were; aeration of the reaction mixture; the concentration of the manganese sulfate was 0.1 mole per liter; a solution containing one equivalence, based on one mole of manganese sulfate, per 2 liters of solution was added to the boiling manganese sulfate at the rate of 26.25 grams per hour per mole of manganese sulfate; the reaction mixture was held at the boiling point for 3 hours after the final addition of potassium permanganate.

Successful adaptation of this synthesis to a continuous reaction basis is indicated by the results of this investigation.

CHEMICAL SYNTHESIS OF BATTERY ACTIVE  
MANGANESE DIOXIDE

by

WILLIAM E. DOMNING

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

for the degree of


Master of Science in Chemical Engineering

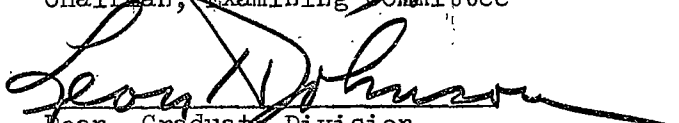
at

Montana State College

Approved:

  
Head, Major Department

  
Chairman, Examining Committee

  
Dean, Graduate Division

Bozeman, Montana  
August, 1955

~~XXXXXXXXXX~~  
N378  
D714c  
Cop. 2

-2-

TABLE OF CONTENTS

Abstract	3
Introduction	4
Specifications	5
Materials and Methods	7
Discussion of Results	16
Summary	38
Literature Cited	41
Acknowledgement	41
Appendix	42

114899

ABSTRACT

A study of the battery activity of the manganese dioxide produced by the oxidation of manganese sulfate by potassium permanganate is presented.

It was the purpose of this work to produce a manganese dioxide from this reaction that would meet drain specifications and to investigate the commercial possibilities of the reaction.

A discussion of the sample preparation and performance of the manganese dioxide produced by this synthesis is given. Chemical analyses, which includes total manganese, available oxygen, moisture content, and pH, are tabulated for each manganese dioxide sample as are apparent density, bobbin weight and initial drain test performance.

A cost analysis of a proposed ten ton per day plant to produce manganese dioxide by the above synthesis is included.

Heat treating of the manganese dioxide made by the above reaction will produce a manganese dioxide that will meet low drain specifications. A suggested method of preparation of a sample by the above procedure is: purification of a technical grade manganese sulfate by the addition of 10 grams of zinc oxide per 124 grams of manganese sulfate, adjustment of the volume of the manganese sulfate solution until the concentration is 88.6 grams per liter, addition, at the rate of 26.25 grams per hour per 124 grams manganese sulfate, of potassium permanganate of a concentration of 52.5 grams per liter. The reaction is to be run at the boiling point. After, washing, filtering and drying the product, it is to be heated for 6 hours at 220 degrees centigrade.

Material meeting both high drain and low drain specifications was produced from technical grade manganese sulfate and potassium permanganate. The conditions of a successful reaction were: aeration of the reaction mixture; the concentration of the manganese sulfate was 0.1 mole per liter; a solution containing one equivalence, based on one mole of manganese sulfate, per 2 liters of solution was added to the boiling manganese sulfate at the rate of 26.25 grams per hour per mole of manganese sulfate; the reaction mixture was held at the boiling point for 3 hours after the final addition of the permanganate.

Successful adaptation of this synthesis to a continuous reaction basis is indicated by the results of this investigation.

## INTRODUCTION

The largest consumption of manganese dioxide is in the manufacture of dry cells, in which it acts as a depolarizing agent. Natural sources of supply of this material are the U.S.S.R., India, Brazil, and West Africa. It is evident that during a war a transportation problem is encountered in the supply of this vital material. Because of the large amount of mobile electronic equipment used by the Army, the demand for large quantities of dry cells is great during a period of emergency.

The Army, through the Signal Corps, has sponsored several research programs to produce, in the United States, a manganese dioxide of suitable depolarizing properties. The first successful process was production by the electrolysis of a manganous sulfate solution. This process, though effective, has the disadvantages of a high operational cost and high power consumption. (Power consumption contributes to the high operational cost, but more important, the use of power is critical during war). Since manganese dioxide may be precipitated by chemical reactions the Army Signal Corps instituted a research program at Montana State College to find a suitable chemical synthesis. The results of three years of research have been reported in works by Berg, et al. (1), Nickelson (6), Davidson (2), Fahlgren (3), Moore (5), Sadogopachari (7), and Kleinfelder (4).

After the conclusion of the Signal Corps contract, the Engineering

Experiment Station at Montana State College decided to continue research in the field. The ultimate object of such research was to be the integration of a chemical synthesis within an existing chemical plant. A survey of the chemical industry disclosed a number of syntheses that could possibly be used. Further study of the more attractive syntheses, which included economic evaluations, indicated that one of the most favorable syntheses was the production of manganese dioxide by the oxidation of manganese sulfate in aqueous solution by the simultaneous reduction of potassium permanganate, whereby the manganese content of both compounds is recovered as battery active manganese dioxide.

The work reported in this thesis includes investigation of methods whereby a specification material could be produced by this synthesis. Previous work had indicated very poor battery performance for material produced from the above starting material, but the very favorable economic climate indicated that a more thorough investigation might be in order. A few large scale reactions are reported in this work.

#### SPECIFICATIONS

Since the largest market for dry cells is the military, the specifications established by the Army Signal Corps for acceptable synthetic manganese dioxide have been used in the evaluation of the samples produced in this investigation. The following specifications are from Bulletin SCL-3117-D (8) dated 18 March 1952.

Chemical Composition

Available oxygen as MnO <sub>2</sub>	85.0% min.
Total manganese as Mn	58.0% min.
Absorbed moisture as H <sub>2</sub> O	3.0% max.
Iron as Fe (soluble in HCl)	0.3% max.
Silicon as SiO <sub>2</sub>	0.5% max.
Total alkalai 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 dioxide 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 dry cells are as follows:

	<u>Low-Drain</u>	<u>High-Drain</u>
Type of discharge	continuous	continuous
Discharge resistance	166-2/3 ohms	16-2/3 ohms
End voltage	1.13 volts	1.00 volts
Temperature	70°F.	70°F.
Relative Humidity	50%	50%
Battery Life	130 hours	5.5 hours

MATERIALS AND METHODS

EQUIPMENT

The small reactions were run in standard laboratory glass equipment. Those pieces of equipment that have been considered unique are described in a following section: SYNTHESES.



In order to run reactions, where the volume would be in excess of the limited size of glass beakers, a 20-gallon reaction vessel was put into use. A Havg lined tank was mounted a sufficient distance above the floor to facilitate product removal. Agitation was provided by a 1/3 h.p. motor belted to a shaft and bearing mount located over the center of the tank. A 6-inch wooden impeller and 3/4-inch wooden driving shaft were coupled to the shaft in the bearing mount. The reaction mixture was heated by a steam sparger. The product was removed either by siphoning or through a bottom bung.

Because the reactions were run at the boiling point, a condenser was provided to remove effluent steam. The condenser was constructed of 10-inch galvanized iron furnace pipe. A section of 10-inch pipe rose directly above the tank to an elbow which contained a blower, which discharged into 6 feet of 7-inch galvanized iron pipe. The 7-inch pipe led downward to a floor drain. The downcoming pipe was packed with 12 inches of Rashig rings and was cooled by two internal water sprays.

Because the quantity of product that was made in the above reaction vessel was larger than ordinary laboratory-size filters could handle, a large suction-type filter was constructed. The filter was made by removing a square portion of the top of a 30-gallon oil drum. The removed portion of the drum was replaced with a piece of filter cloth held in place by bolted wooden cleats. The bottom of the drum was fitted with a drain valve. A hole was cut in the side of the drum 12 inches from the top. A piece of 1/2 inch pipe was brazed in this hole and was connected

to a Nash "Hytor" vacuum pump. In operation, a slurry is poured on the cloth and is filtered by vacuum.

### Reagents

Since the goal of this investigation was to develop a process that could be integrated in a commercial plant; both C. P. grade and Tech. grade chemicals were used. The C.P. grade chemicals were used where it was desired to produce an oxide of high purity for battery evaluation. The Tech. grade chemicals were used where it was desired to determine the effect of the impurities on the battery life of the product, and in the larger scale reactions. No work was done with natural ores because the main plant was expected to supply both reagents of Tech. grade purity.

### Syntheses

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

1. Solutions of the reactants were made.
2. The manganous sulfate solution was heated to the boiling point in either a 20 liter Pyrex jar or in the large reaction vessel.
3. The  $\text{KMnO}_4$  solution was added to the hot  $\text{MnSO}_4$  solution at the desired rate.
4. The reaction mixture was allowed to agitate for a desired length of time after the completed addition of the  $\text{KMnO}_4$ . The temperature may have been maintained at the boiling point or the solution may have been allowed to cool.
5. Decantation of the reaction effluent and subsequent additions and decantations of wash water was carried out. The sample was washed until the pH of the effluent wash water reached 6.5 - 7.0.

6. The sample was filtered and transferred to a drying oven.
7. The drying time, at a temperature of 105 to 110°C., was approximately 48 hours for each sample.
8. The sample was next ball-milled for 2 hours in a 3.5 gallon size porcelain pebble mill revolving at 60 rev./min. and charged with approximately 5.5 lb. of flint pebbles of about one-inch diameter each.
9. Upon removal from the ball-mill, the sample was screened through a U. S. Standard Sieve No. 40, the -40 mesh portion being retained and stored for testing.
10. The necessary analytical tests were carried out on the sample. (See Table I in the Appendix).
11. "A" size cells were fabricated out of the sample.
12. The fabricated cells were tested at each specified resistance. The number of cells that were tested on each resistance varied. Enough cells were tested such that at least two cells had approximately equal drain lives.

Notes for steps 2-4: the reaction mixture is under constant mechanical agitation; the reaction is maintained at constant volume by the addition of hot H<sub>2</sub>O; the Pyrex vessel was heated by an electric immersion heater and a hot plate; the large reaction vessel was heated by sparged steam.

Those samples whose numbers are suffixed by the symbol "H", were made by heating the sample in an electric oven at the desired temperature and for the desired length of time.

The main variables encountered in this investigation are: concentration of reactants, time of reaction, effect of external agents, and purity of reactants. These variables are correlated with battery activity in the discussion section of this thesis. Complete studies of each of the

above variables have not been made. Because of the nature of the problem, as outlined in the introduction, the research was planned so that a change of variables would produce a significant change in the battery life. All reactions, except one, were batch reactions, the one exception being run on a semi-continuous basis.

#### Battery Fabrication and Testing

From 5 to 10 standard "A" size dry cells were constructed in accordance with cell assembly techniques outlined in Army Signal Corps specifications Bulletin SCL-3117-D (8). A mixture containing 80 percent by weight of the manganese dioxide sample, 8 percent Shawinigan carbon black, and 12 percent  $\text{NH}_4\text{Cl}$  was blended in a pebble mill for 20 minutes to assure uniform consistency. This mixture was dampened with a wetting solution consisting of 5.8 percent  $\text{NH}_4\text{Cl}$  by weight, 8.6 percent  $\text{ZnCl}_2$ , and 85.6 percent  $\text{H}_2\text{O}$  until material acceptable for tamping was obtained.

From the mixture described above, bobbins were tamped in an apparatus which is diagrammatically shown in 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.

After tamping, 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 consisting of 23.7 percent  $\text{NH}_4\text{Cl}$ , 22.3 percent  $\text{ZnCl}_2$ , 0.1 percent  $\text{HgCl}_2$ , and 53.9 percent  $\text{H}_2\text{O}$  to 10.7 gm. of

a mixture containing 74.7 percent cornstarch 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 wax.

After a period of five days, the cells were screened for open voltage and then from 4 to 6 cells were discharged through the previously specified resistances. Figure 2 of the Appendix schematically shows a portion of the test rack. 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 resistance, called low drain (L.D.); and 1.00 volts for the 16.67 ohm resistance, called high drain (H.D.).

The voltmeter in the test rack consisted of a Simpson 50 micro-ampere ammeter in series with a 330,000 ohm carbon resistor and a 10,000 ohm variable resistor. By adjustment of the variable resistor, it was possible to calibrate the ammeter, against a standard voltmeter, such that voltages between 1.00 and 1.20 could be read directly from the meter's scale. The meter could be read to an accuracy of  $\pm .005$  volts. The calibration of the ammeter, used as a voltmeter, was tested periodically by measuring the voltage of a standard cell on the open voltage circuit. It was found that the calibration of the ammeter remained constant. The use

of an ammeter as a voltmeter has 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 Army Signal Corps specification of 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 (8). The determination was made as follows:

A sample of dried ore (approximately 0.2 gm.) was weighed accurately into a 600 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 stock solution to serve as a control. Both the original and control sample were diluted to 150 ml. with deionized 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 adjusted to about 200 ml. The samples were then titrated with a solution of potassium dichromate of known concentration (approximately 0.2N) using the potentiometric method

for detection of end point.

#### Total Manganese Analysis

A sample of dried ore (approximately 0.1-gm.) was weighed accurately into a 600 ml. beaker fitted with a watch glass. Ten ml. of distilled water and 5 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 and 10 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. deionized water and 3 gm. of sodium bismuthate were added. The mixture was stirred for five minutes and filtered, with suction, through a fine sintered-glass filter funnel into a one-liter side arm flask. The filter funnel, containing excess bismuthate, was washed several times with deionized water to assure removal of the manganate ion. Fifty ml. of sodium oxalate solution (approximately 0.2 N) and 100 ml. of 10% sulfuric acid were added to the solution. This solution was heated almost to boiling and the excess oxalate was titrated with 0.1 N potassium permanganate.

#### pH Determination

A one gram sample of the dried ore was accurately weighed into a 250 ml. Erlenmeyer flask and a quantity of deionized water equal to exactly 100 times the weight of sample 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 then fitted with drying tubes containing ascarite and the mixture allowed to cool 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. During the pH measurement, the beaker containing the sample was stirred to obtain a uniform suspension of the solids.

#### Apparent Density

Apparent density was determined by running a portion of the -40 mesh 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 from 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. This data was 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

##### Cost Analysis of the Process

As was mentioned in the introduction, this process has the advantage of a favorable economic climate. To further illustrate this point, a condensed cost analysis of the reaction scheme is given below.

The reaction is:  $3\text{MnSO}_4(\text{aq.}) + 2\text{KMnO}_4(\text{aq.}) + 2\text{H}_2\text{O}(\text{l.}) \xrightarrow{\Delta} 5\text{MnO}_2 \cdot x\text{H}_2\text{O}(\text{s.}) + \text{K}_2\text{SO}_4(\text{aq.}) + 2\text{H}_2\text{SO}_4(\text{aq.})$ . The process to be used is the batchwise addition of  $\text{KMnO}_4$  to  $\text{MnSO}_4$  at the boiling point.  $\text{ZnO}$  will be added to the  $\text{MnSO}_4$  for purification. The reaction mixture will be aerated but mechanical agitation will also be used. Washing will require a three stage counter-current decantation unit. The precipitated product will be filtered on a rotary drum filter and dried in a kiln-type dryer. Pebble-milling of the dried product will be done with porcelain equipment. The necessary analyses and tests will be performed on the product before sale.

It will be assumed that the main plant will be able to supply the manganese dioxide process with  $MnSO_4$  and  $KMnO_4$ . No credit will be taken for the secondary reaction products. Recovery of manganese will be assumed to be 95 percent of input. Buildings, land, and necessary dockage facilities will not be considered as part of the required investment. Handling and transportation losses will be ignored because hydration of the product  $MnO_2$  will make up for such losses.

Market studies, by the Army Signal Corps, have shown that the battery industry would buy about 10 tons per day of a salable product at \$0.25 per pound. The cost of the reagents are those prices found in the recent issues of "Chemical and Engineering News".

This study is divided into the following sections: plant cost, operating cost, and investment. Each of these sections shows the necessary calculations pertinent to the desired result. A summary of the complete analysis is given at the end of the study.

Plant Cost:

1	Two mixing tanks, wood, 2000 gallons.	\$ 4,000
2	Two reaction vessels, asphalt lined wood tanks, 10,000 gallons with heating coils and agitation equipment.	12,000
3	Countercurrent decantation unit, 3 thickeners and 3 slurry tanks.	12,000
4	Rotary filtration equipment, 200 sq. ft. of filtering area.	12,000
5	Rotary product dryer.	5,000

Pebble-mill and classifier	\$ 12,000	
Total equipment cost.	<u>\$ 57,000</u>	
Installation of equipment, 50 percent of equipment cost.	\$ 28,500	
Piping, pumping and transportation equipment, 30 percent of equipment cost.	17,100	
Materials handling equipment.	<u>10,000</u>	
Total cost of plant equipment.	<u><u>\$ 112,600</u></u>	464,549

Operating Costs:

Reagent Cost:

$$20,000 \frac{\text{lb.}}{\text{day}} \times \frac{55 \text{ lb. Mn.}}{87 \text{ lb. MnO}_2} \times \frac{1}{0.95} = 13,310 \frac{\text{lb.}}{\text{day}}$$

$$13,310 \frac{\text{lb.}}{\text{day}} \times \frac{3}{5} \times \frac{151 \text{ lb. MnSO}_4}{55 \text{ lb. Mn.}} = 22,000 \frac{\text{lb. MnSO}_4}{\text{day}}$$

$$13,310 \frac{\text{lb.}}{\text{day}} \times \frac{2}{5} \times \frac{157 \text{ lb. KMnO}_4}{55 \text{ lb. Mn.}} = 15,200 \frac{\text{lb. KMnO}_4}{\text{day}}$$

$$22,000 \frac{\text{lb. MnSO}_4}{\text{day}} \times \frac{1 \text{ lb. ZnO}}{50 \text{ lb. MnSO}_4} = 400 \frac{\text{lb. ZnO}}{\text{day}}$$

	<u>Reagent</u>	<u>lb./day</u>	<u>Cost \$/lb.</u>	<u>Total cost/day</u>	
\$145/ton	MnSO <sub>4</sub>	22,000	\$ 0.01 0.05	\$ 220	665 1100
\$1.96/kg	KMnO <sub>4</sub>	15,200	0.15 0.89	2,280	13528
47.5¢/lb	ZnO	440	0.15 0.475	66	209
				<u>\$ 2,566</u>	14,837
				10,586	10,586

Reagent cost per pound of finished product:

$$\frac{\$ 2566/\text{day}}{20,000 \text{ lb./day}} = \$ 0.1281 / \text{lb.} \quad \underline{0.1281} \approx 0.13$$

Process Energy Cost:

There are 236,300 lb. of aqueous reaction mixture to be heated per day. The heat capacity of the mixture will be assumed approximately equal to 0.9  $\frac{\text{B.t.u.}}{\text{lb. of}}$

$$236,300 \times 0.9 (212 - 62) = 31,900,000 \text{ B.t.u.}$$

Ten percent of the above heat will have to be replaced in the system because of heat losses. Sixty percent heat transfer will be attained.

$$\frac{31,900,000 \times 1.1}{0.6} = 58,500,000 \text{ B.t.u./day}$$

It will be assumed that the filter cake will contain 20 percent moisture. This will necessitate the removal of 5,000 lb. water per day. Heat of vaporization equals 1000 B.t.u./lb/ H<sub>2</sub>O.

$$\frac{5000 \times 1000}{0.6} = 8,350,000 \text{ B.t.u./day}$$

Total heat required, per day, is 66,850,000 B.t.u.

Cost of heat is  $\$ \frac{4.00}{10^6} / 1.05 \times 10^6$  B.t.u.

$$66,850,000 \times \frac{\$ 0.895}{1.05 \times 10^6} \times \frac{1}{20,000} = \$ 0.0029/\text{lb.}$$

The cost of electricity will be included in the miscellaneous costs, which will be set at \$ 0.01 per pound of finished product.

Summary of reagent and processing costs per pound of MnO<sub>2</sub>.

Reagents	\$ 0.1281	0.53
Heat	0.0020	1.3
Miscellaneous	0.01	0.04
Total	\$ 0.1410/lb.	0.583 /lb

Fixed Operating Cost:

Direct Labor:

		<u>Cost/day</u>	
9 Operators \$2.50/hr.	12.5	\$ 180.00	864
4 Laborers \$1.75/hr.	12.5	56.00	864
3 Maintenance \$2.75/hr.	12.5	66.00	864
1 Chemist \$385/mo.	1500	13.00	72
3 Technicians \$300/mo.	1200	30.00	57
		<u>\$ 345.00</u>	<u>2731</u>
Employee benefits (13%)		45.00	855
Total direct labor		<u>390.00</u>	<u>3086</u>

Expenses:

1 Chemical Engineer \$450/mo.	2500	15.00	119
1 Salesman \$10,000/yr.	2000	28.00	95
Office and Administrative expense.		165.00	500
Depreciation (7½ years).		45.00	172
Repair materials.		10.00	30
Building rent.		<del>10.00</del>	
Burden l.		195.00	600
Total expenses (120% direct labor).		<u>468.00</u>	<u>1516</u>

Total fixed operating cost. \$ 858.00    4602

$\frac{\$ 858/\text{day}}{20,000 \text{ lb/day}} = \$ 0.0429/\text{lb.} \quad 0.2301$

Total manufacturing cost equals the sum of the material, labor and expense costs.

Material cost	\$ <del>0.1410</del>	0.583
Labor and expense	<u>0.0429</u>	<u>0.2301</u>
Total manufacturing cost	<u>0.1839</u>	
Freight	<u>0.01</u>	<u>0.025</u>
Total cost, F. O. B. battery fabrication plant, per lb.	<u>\$ 0.1939</u>	838

$$87.5 - 83.8 = 3.7$$

Gross profit equals selling price less cost.

Selling price \$ 0.25/lb. - \$ 0.1939/lb. = \$ 0.0561/lb.

1. Burden consists of unforeseen expenses, local taxes and contributions for the supply of utilities.

\$ 0.0561/lb. x 7,300,000 lb./yr. = \$ 401,000/yr.

Gross profit	\$ 401,000	
Less:		
Property tax (3%)	4,368	\$ 396,632
Income taxes (52%)		<u>209,000</u>
Net profit per year		\$ 187,632

Investment:

Listed below is the estimated initial investment requirement for a ten ton per day plant.

Fixed assets (Plant cost)		\$ 112,600
Development		20,000
Inventory:		
MnSO <sub>4</sub>	\$ 2,000	
KMnO <sub>4</sub>	15,000	
ZnO	1,000	
Finished Goods	<u>15,000</u>	<u>33,000</u>
Accounts Receivable		150,000
Accounts Payable		50,000
Cash		<u>50,000</u>
Total investment required		<u>\$ 415,600</u>

The return on the required investment for a selling price of

\$ 0.25 per pound is:

$\frac{\$ 187,632}{\$ 415,600} \times 100 = 45 \text{ percent.}$

Summary:

The actual cost of a plant that would produce 10 tons per day of battery active manganese dioxide by the potassium permanganate oxidation

of manganese sulfate is \$ 112,600. It will cost about \$ 0.1939 per pound to produce battery active manganese dioxide by this synthesis and deliver it to a battery fabricator. The net profit per year will be in the order of \$ 187,632 and will represent 45 percent of an estimated capital requirement of \$ 415,600.

#### The Potassium Permanganate Oxidation of Manganous Sulfate

Methods of preparation and analytical and test data for the manganese dioxide specimens produced in this study are shown in the Appendix, Table I and Table II. An code was used to designate different samples, the first letter, S, denotes manganese sulfate, the second group, KP, denotes potassium permanganate, and the number differentiates the reactions. The suffixing of the letter, H, after the number indicates heat treatment of a portion of the sample, the letters, HS, denotes hydrogen sulfide treatment, while the addition of lower case letters differentiates subsequent treatments.

This study was termed the S-KP synthesis. The general chemical equation is:  $3\text{MnSO}_4 (\text{aq.}) + 2\text{KMnO}_4 (\text{aq.}) + 2\text{H}_2\text{O} (\text{l.}) \xrightarrow{\Delta} 5\text{MnO}_2 \cdot x\text{H}_2\text{O} (\text{s.}) + \text{K}_2\text{SO}_4 (\text{aq.}) + 2\text{H}_2\text{SO}_4 (\text{aq.}).$

These reactions of this synthesis were carried out in the manner described in the section, "Materials and Methods."

Previous work reported by Berg et al. (1), and Kleinfelder (4), indicated that the product of an S-KP reaction gave an unfavorable drain life. Kleinfelder (4) indicated that specification manganese dioxide

could not be produced from the S-KP reaction at concentrations of from 0.0625 to 1.0 moles of manganese sulfate per liter of reaction volume. This information suggested treatment of the product manganese dioxide to upgrade its drain life. One treatment known to be of value was the low temperature heating of manganese dioxide. This treatment was tried on the remaining product of reaction S-KP-5 and designated sample S-KP-5H. This sample had 2.25 hr. H. D. and 146 hr. L. D.

Since sample S-KP-5 was made by Kleinfelder (4), its method of preparation is given below.

" Dissolved 160 gm.  $MnSO_4 \cdot H_2O$  in 1 liter  $H_2O$ ; heated to  $85^\circ C$ .; added, dropwise, over a 2.25 hr. period, 105 gm.  $KMnO_4$  in 2 liters  $H_2O$ . Reaction volume was maintained at 1 liter. Reaction time was 6 hr. at an average temperature of  $85^\circ C$ . The reaction mixture was cooled, with agitation, for 16 hr. before washing. The product was ball-milled for 2 hr. after drying."

Because of the success of sample S-KP-5H it was decided to investigate further, the reaction variables and heat treating of samples.

#### Reaction Concentration Study

Kleinfelder (4) reports five reactions in which the concentrations of the reactants were varied. These reactions (S-KP-1, 2a, 3, 4, and 5) of his will be used in this study along with reactions S-KP-6, 7, 8, 15, 16, and 17.

Table III and Figure 4 in the Appendix show the effect of total reaction volume. The curve in Figure 4 indicates that a dilute solution of manganese sulfate should be used. Although none of the samples met specifications, drain variance was from 1.0 to 4.4 hr. H. D. and 50 to



124 hr. L. D. The total reaction volume was varied from one liter to 40 liters per mole of manganese sulfate.

The fact that a better drain test arises from the use of a dilute solution of manganese sulfate is shown in Table IV and Figure 5 in the Appendix. The above table and figure show the effect of concentration of manganese sulfate at constant concentration of potassium permanganate. The basis for comparison has been taken as one equivalence of potassium permanganate per mole of manganese sulfate per two liters of solution. Sample S-KP-17, having a concentration of 0.025 mole of manganese sulfate per liter of solution, shows the best drain test with 4.0 hr. H. D. and 106 hr. L. D.

Table V and Figure 6 in the Appendix show the effect of the concentration of potassium permanganate based on a concentration of manganese sulfate of one mole per seven liters of solution. Two concentrations of potassium permanganate, 0.57 and 1.1305 mole equivalents (based on one mole of manganese sulfate), were used for this study. The product of the more concentrated solution had the better drain test (1.9 hr. H. D., 55 hr. L. D. vs. 0.9 hr. H. D., 42 hr. L. D.). The quantity and scope of the data presented in this study prevent the postulation of a principle.

The study of the effect of the concentration of the reactants has shown that, while no specification material was produced, the best drain tests occurred at the more dilute concentrations on manganese sulfate e. g. about 0.025 moles per liter. Although a concentration

of 1.1305 mole equivalents per liter of potassium permanganate was the better of the two concentrations chosen for study, the data is too limited to warrant a definite conclusion.

#### Reaction Time Study

Reactions S-KP-1, 8, 9, and 10 were used to study reaction time. The concentration of manganese sulfate was held constant at one mole per 16 liters. The basis for comparison of the drain date for the above reactions will be taken as the time required to add 105 grams of potassium permanganate to the reaction. A 2.5 hr. addition time gave a drain test of 2.0 hr. H. D. and 78 hr. L. D. while a 4 hr. addition time gave a drain test of 4.4 hr. H. D. and 124 hr. L. D. An addition time of 10 hr. gave a drain test of 4.0 hr. H. D. and 106 hr. L. D. while a 15 hr. addition time gave a drain test of 4.3 hr. H. D. and 90 hr. L. D.

This limited study shows that the time of addition of potassium permanganate is critical if its rate of addition is rapid. For slower rates of addition, not too great an effect is evident. Within the limitations of this study, the optimum rate of addition appears to be 26.25 grams of potassium permanganate per hour per mole of manganese sulfate.

Reactions S-KP-28 and 19 were run with the same concentrations of reactants: 0.6 mole manganese sulfate per gallon of solution and 52.5 grams of potassium permanganate per liter of solution. The rate of addition of the permanganate for reaction S-KP-19 was 26.25 grams per hour per mole of manganese sulfate. The rate of addition of permanganate

to reaction S-KP-28 was 35 grams per hour per mole of manganese sulfate. The discrepancy in the drain tests of the two samples is apparent; S-KP-19 (26.25 gm. per hr. per mole  $MnSO_4$ ) had drain tests of 4.75 hr. H. D. and 76 hr. L. D. while the drain tests for S-KP-28 (35 gm. per hr. per mole  $MnSO$ ) were 0.81 hr. H. D. and 58 hr. L. D. These two reactions indicate that the best rate of addition of potassium permanganate is 26.25 grams per hour per mole of manganese sulfate.

#### Other Reaction Variables

The variable of temperature was not evaluated because work done by previous investigators, Berg et al. (1), had shown that inactive material had been formed when the reaction was run at temperatures lower than the boiling point.

The time of ball-milling of the manganese dioxide was not investigated because work done by Kleinfelder (4) had shown the percent increase in drain life to be small for an increased ball-milling time over 2 hr.

Reaction S-KP-11 was run to determine the effect of enlarging the reaction size on the drain life of the product. Reaction S-KP-11 was run under conditions identical to S-KP-3. Twice the amount of reagents were used in S-KP-11 as were used in reaction S-KP-3. The concentration of manganese sulfate was one mole per two liters of solution, the concentration of potassium permanganate was one equivalence (based on one mole of manganese sulfate) per two liters of solution. The rate of addition of the permanganate was 52.5 grams per hour per mole of manganese sulfate. The results of S-KP-11 (1.4 hr. H.D. and 60 hr. L.D.) were essentially the same as

S-KP-3 (1.5 hr. H. D. and 44 hr. L. D.). This indicates that the larger reaction size does not have an effect on the product of the reaction provided all variables are the same in each instance.

#### Heat Treating Study

The heat treating of the products of the S-KP synthesis was initiated with sample S-KP-5H. The conditions for the heating were 9 hr. at 310°C. The success of sample S-KP-5H (2.25 hr. H. D., 146 hr. L. D. vs. 0.3 hr. H. D., 20 hr. L. D. for S-KP-5) prompted heat treating of subsequent samples at conditions similar to those of S-KP-5H. A portion of succeeding reactions was heat treated. The heat treating of samples of reactions S-KP-6 through 21, with the exception of reactions S-KP-13, and 19, was carried out for 9 hr. at 310°C. Most of the samples made by treating manganese dioxide in this manner did not give an appreciably improved drain test over the original product. Those samples which met or nearly met specifications will be noted. Sample S-KP-8H met the low drain specification with a drain test of 134 hr. Sample S-KP-8 was made with a concentration of 0.0724 mole manganese sulfate per liter of solution, potassium permanganate of the concentration, 0.38 mole per liter of solution, was added at a rate of 26.25 grams per hour per mole of manganese sulfate. S-KP-5, whose heat treated analog met the low drain specification, was made from manganese sulfate of a concentration of one mole per liter of solution. Potassium permanganate for the foregoing reaction was of the concentration 0.332 mole per liter of solution and was added at a rate of 42 grams per hour per mole of manganese sulfate. Sample S-KP-8

differed from sample S-KP-5 with respect to concentration of all reactants and rate of addition of potassium permanganate. Despite the difference, the heat treated portions of each reaction met the low drain specification. Samples S-KP-8, 13, and 14 were made in the following manner: The concentration of manganese sulfate was 0.0724 mole per liter, potassium permanganate was added at a rate of 26.25 grams per hour per mole of manganese sulfate, the concentration of the permanganate was 0.38 mole per liter of solution. Since samples S-KP-8H and 14H were prepared by heating a portion of the analogous oxidation reaction product for 9 hr. at 310°C., the drain tests for these samples should be in close agreement. The drain tests for S-KP-14H were 3.5 hr. H. D. and 128 hr. L. D. which closely approaches the drain life of S-KP-8H (4.0 hr. H. D., 134 hr. L.D.). Sample S-KP-13 was made with technical grade chemicals and sample S-KP-13H was made by heating a portion of sample S-KP-13 for 20 hr. at 310°C. The drain tests for sample S-KP-13 were 3.6 hr. H. D. and 35 hr. L. D.

Reaction S-KP-19 was made by combining potassium permanganate of a concentration of 52.5 grams per liter of solution with manganese sulfate of a concentration of 0.6 mole per gallon of solution at a rate of 26.25 grams per hour per mole of manganese sulfate. The product of reaction S-KP-19 was divided into nine 70 gram portions, each of which was given a different heat treatment. Table VI and Figure 7 in the Appendix show the effect of the temperature of heating on the drain life of S-KP-19. The temperatures chosen were 230, 265, 310, and 355°C. The temperature of 230°C. damaged the original product least (4.0 hr. H.D., 77 hr. L. D. vs.

4.75 hr. H. D., 76 hr. L. D. for S-KP-19). Table VII and Figure 8 in the Appendix show the results of a varied heating time on sample S-KP-19. Heating times of 3, 6, 15, and 24 hours were tried. The temperature was constant at 305°C. As before none of the heat treated samples showed improvement over the original life of S-KP-19. The heating time of six hours yielded a product whose drain test closely approached that of the original product (4.6 hr. H. D., 62 hr. L. D. vs. 4.75 hr. H. D., 76 hr. L.D.). To test the results of the above studies, sample S-KP-19Hi was made. This sample was heated at a temperature of 238°C. for 6 hr. In comparison with sample S-KP-19, sample S-KP-19Hi had a test of 0.25 hr. less on high drain and a low drain test of 5 hr. longer than S-KP-19.

Although the results of the foregoing study were not definitely conclusive, a heating time of 6 hr. and a temperature of 220°C. was chosen for all remaining heat treatments. Samples S-KP-29H and 30H should have had low drain tests meeting or nearly meeting low drain specifications. These two reactions duplicated the method of preparation of successful reactions S-KP-8H and 14H. (The conditions for these reactions are given below.) The drain tests for reaction S-KP-29H were 1.0 hr. H. D. and 44 hr. L. D. while the drain tests for S -KP-30H were 1.5 hr. H. D. and 166 hr. L. D. An unpurified manganese sulfate was used for reaction S-KP-29. The poor performance of S-KP-29H indicates the necessity of purification of the manganese sulfate before oxidation for the production of specification grade material.

It may be concluded that a method of producing battery active

manganese dioxide that will meet low grain specifications has been developed. The suggested procedure is that for S-KP-30H. and is as follows:

Reactants: Technical grade manganese sulfate and potassium permanganate. The manganese sulfate is to be purified by the addition of 10 gm. zinc oxide per 124 gm. pure manganese sulfate.

Concentration: Manganese sulfate- 88.6 gm. per liter. Potassium permanganate- 52.5 gm. per liter.

Addition: 26.25 gm. potassium permanganate per hour per 124 gm. pure manganese sulfate.

Temperature: Approximately 90°C.

Cooling: Cool, with agitation, for 16 hr. before filtering.

Washing: Wash until the pH of the effluent washwater is between 6.8 - 7.0.

Drying: Dry product at 110°C. for 48 hr.

Heating: Mortar the dried product, treat the -40 mesh material in a muffle furnace for 6 hr. at 220°C.

It should be pointed out that the temperature used for treating the samples is that temperature in the free space of the muffle furnace in which heat treating of the above samples took place. The time of heating, suggested above, is that time found to be most favorable for a 70 gm. sample. It is suggested that the time of heating and the temperature of heating for different sized samples may be different than the results of this study.

#### Adaptation of Commercial Reagents to the Reaction

Technical grade reagents were used in three reactions in an attempt to evaluate the commercial adaptability of the reaction. The reactions used for this study were S-KP-12, 13, and 14. S-KP-12 had the following reaction conditions: the concentration of manganese sulfate was one mole per two liters of solution, the concentration of potassium permanganate

was one equivalent (based on one mole of manganese sulfate) per two liters of solution. The rate of addition of the permanganate was 52.5 grams per hour per mole of manganese sulfate. These conditions are the same conditions specified for reactions S-KP-11 and 3. The above reaction conditions were picked because S-KP-11 had been a close duplication of S-KP-3 and thereby, the drain test of S-KP-12 could be predicted. S-KP-12 had a drain test of 2.5 hr. H. D. and 42 hr. L. D., which compared closely with S-KP-11 with a drain test of 1.4 hr. H. D. and 60 hr. L. D. The proximity of the above values of the drain tests indicated that the impurities in the manganese sulfate supplied by the Carus Chemical Co. of LaSalle, Illinois, were not detrimental to battery life.

To further investigate this hypothesis, reactions S-KP-13 and 14 were run. The conditions for these two reactions were the same as those for reaction S-KP-8. They are as follows: Concentration of 0.0724 mole manganese sulfate per liter of solution, 0.38 mole per liter of solution of potassium permanganate, added at a rate of 26.25 grams per hour per mole of manganese sulfate. Reaction S-KP-8 was made using C. P. grade chemicals; reaction S-KP-13 used technical grade reactants; reaction S-KP-14 used a purified technical grade manganese sulfate and technical grade potassium permanganate. Zinc oxide was chosen as the purification agent because any ionic zinc compounds formed during the purification would act as a catalyst to the oxidation reaction, Berg et al. (1).

As would be expected, the sample made from purified manganese sulfate had a slightly higher drain life, e. g. S-KP-13, 4.25 hr. H. D., 110 hr. L. D.,



S-KP-14, 4.6 hr. H. D., 122 hr. L. D. Both reactions produced samples that had drain lives close to that of sample S-KP-8 (4.4 hr. H.D., 124 hr. L.D.). Reaction S-KP-14 then becomes a duplication of reaction S-KP-8, while the results of reaction S-KP-13 show that purification of the manganese sulfate is unnecessary.

It is possible to conclude, from this brief study, that the purification of commercial grade manganese sulfate is not necessary to make specification battery active manganese dioxide. (Based on manganese sulfate manufactured by the Carus Chemical Co.)

#### Other Methods

From the foregoing studies, it is evident that only one method of producing specification battery active manganese dioxide has been found. Although a full investigation of reaction variables was not completed, it was felt that enough work had been done to substantiate the hypothesis that in order to make specification battery active manganese dioxide by the S-KP reaction, it shall be necessary to introduce an additional step into the reaction sequence.

The various methods tried are listed below.

#### Hydrogen Sulfide Adsorption-Desorption

Sample S-KP-6H-HS was made to determine the effect of adsorbing and then desorbing hydrogen sulfide gas on manganese dioxide. This sample was prepared by suspending 100 grams of sample S-KP-6H in 3 liters of water and 30 cc. of phosphoric acid (sirupy). Hydrogen sulfide gas was bubbled into the mixture until an appreciable color change was noted. The sample was

filtered and placed in a muffle furnace at 300°C. for 2 hr. Because the drain test, after treating was not greatly improved over sample S-KP-6H, no more samples were made by this process.

#### Hydrochloric Acid Leach

Berg et al. (1) lists a method of treating manganese dioxide with hydrochloric acid, whereby the battery life of the manganese dioxide is improved. Using the above method of leaching, two samples were made; S-KP-11a and 12a. The drain life of each of these samples was less than that of the original sample and for this reason, further work was not undertaken.

#### Ammonium Hydroxide Digestion

Digestion of sample S-KP-16 in ammonium hydroxide was tried. Approximately 200 grams of S-KP-16 was digested in a solution of 100 cc. conc. ammonium hydroxide in 3 liters water. This digestion proved detrimental to both high drain and low drain battery life, relative to the original sample.

#### Incorporation of an Acid in the Reaction Mixture

Four reactions were run in this series; two reactions using hydrochloric acid and two reactions using nitric acid. They are reactions S-KP-20, 21, 22, and 23. The concentration of manganese sulfate (one mole per 2 liters of solution) and potassium permanganate (one equivalence per mole of manganese sulfate per 2 liters of solution) was constant throughout this series, as was the method of preparation. One-tenth mole and 0.25 mole of hydrochloric acid per mole of manganese sulfate, were added to reactions S-KP-20 and 21 respectively. The drain tests for these two reactions are:

S-KP-20, 1.05 hr. H.D., 37 hr. L.D.; S-KP-21, 2.3 hr. H.D., 50 hr. L.D. One-tenth mole and 0.25 mole of nitric acid per mole of manganese sulfate, were added to reactions S-KP-22 and 23 respectively. The drain tests for these two reactions are: S-KP-22, 2.3 hr. H.D., 87 hr. L.D.; S-KP-23, 1.0 hr. H.D., 38 hr. L.D.

None of the samples had drain tests which met specifications. Further study was not made.

#### Conversion of the Manganese Sulfate to Manganese Chloride

Kleinfelder (4) was successful in producing specification battery active manganese dioxide using manganese chloride and potassium permanganate. Reaction S-KP-31 was run by oxidizing manganese chloride (made by treating manganese sulfate with calcium chloride) with potassium permanganate by a method outlined by Kleinfelder (4). The drain test of sample S-KP-31 was 1.0 hr. H.D. and 57 hr. L.D.

Since the usual S-KP synthesis contains one less step, the process involving the conversion of the sulfate to the chloride does not appear as favorable as the direct oxidation from the economic standpoint.

#### Incorporation of Carbon Black in the Reaction Mixture

In an attempt to evaluate the effect of surface on the formation of gamma phase manganese dioxide, carbon black was added to reaction S-KP-32. Except for the addition of the carbon black, reaction S-KP-32 is a duplicate of reaction S-KP-8. One equivalence (per mole of manganese sulfate) of potassium permanganate in two liters of solution was added to one mole of manganese sulfate in 16 liters of solution. Fifteen grams of carbon black

were suspended in the manganese sulfate solution.

Despite the fact that the carbon black was not removed before fabrication of the sample into cells, the drain life of 2.5 hr. H.D. and 111 hr. L.D., for sample S-KP-32, closely approaches the drain life of S-KP-8 (4.4 hr. H.D., 124 hr. L.D.)

#### Aeration of the Reaction Mixture

In order to agitate a reaction mixture (S-KP-18), air was bubbled into the reaction. Sample S-KP-18 was prepared in a reaction vessel containing 8000 grams of flint pebbles. The concentration of reactants was 0.1 mole manganese sulfate per liter of solution, one equivalence ( $\text{KMnO}_4$ ) per mole of manganese sulfate per 2 liters of solution. The rate of potassium permanganate addition was 70 grams per hour per mole of manganese sulfate. The reaction mixture was air agitated. The product from this reaction, when fabricated into cells and tested, had a drain life of 5.51 hr. H.D. and 125 hr. L.D. Because sample S-KP-18 met the high drain specification and was only 5 hr. short of the low drain specification, reaction S-KP-24 was formulated to try to determine the effect of aeration on the battery activity of manganese dioxide produced by the S-KP synthesis. The reaction conditions for S-KP-24 were identical to those of S-KP-18 except for the presence of the pebbles. The drain life of the product of this reaction was 5.4 hr. H.D. and 126 hr. L.D. The battery tests of S-KP-24 duplicate the tests of reaction S-KP-18. From this information it was assumed that the presence of air in the reaction mixture is beneficial to the drain life of manganese dioxide produced by the S-KP synthesis.

Because the above two samples did not meet both drain specifications, and earlier work had indicated the importance of manganese concentration, a series of three reactions, S-KP-25, 26, and 27 were run at concentrations of one mole of manganese sulfate per 2, 6, and 14 liters of water respectively while the concentration of permanganate was constant at one equivalence per mole of manganese sulfate per two liters of solution. It was the purpose of this series to determine the function of manganese concentration in the aerated reaction. The battery drain tests for the above reactions are as follows: S-KP-25, 4.5 hr. H.D., 61 hr. L.D.; S-KP-26, 4.7 hr. H.D., 118 hr. L.D.; S-KP-27, 5.0 hr. H.D., 150 hr. L.D. Sample S-KP-27 exceeded the low drain specification by 20 hr. It is evident from this study that the concentration of manganese sulfate, one mole per 14 liters of solution, used in reaction S-KP-27, is the most favorable concentration used. The conclusion to this study is in accord with a similar study presented in an earlier section of this thesis.

The effect of impurities in the manganese sulfate was studied by reactions S-KP-29 and 30. The preparation of both samples is identical to the preparation outlined for reaction S-KP-27. Sample S-KP-29 was made from technical grade manganese sulfate supplied by the Carus Chemical Co., while sample S-KP-30 was made from purified (zinc oxide method) manganese sulfate. The drain tests for these reactions are: S-KP-29, 4.5 hr. H.D., 114 hr. L.D.; S-KP-30, 3.75 hr. H.D., 96 hr. L.D. The sample prepared from the impure manganese sulfate gave the greater drain test.

In the light of studies made on the aeration of the reaction mixture





































































