729843

		deg/900	T
(1)	250 hrs —	3%	15°C
(2)	"	11-13	30°C
(3)	our work	15?	25°C

R

(4) bubbled O_2 through (39% milled) complete inactivity

(a) in 106 hrs — red no cycling O_2 present

(b) same except 10% unmilled 5% loss

(c) 100 hrs with 30-95° cycles no color. no O_2 present stirred - no gas flow.

BEST COPY AVAILABLE

.2 micron

.2 $\times 10^{-4}$

2×10^{-5} cm.

(1) [illegible]

(2) X ray

(3) wearing [illegible] before cycling

1259993

Dr. Calvin —

Comment on Dupont report.

(1) no evidence that they ever carried out grinding in absence of air

(2) Could one grind pyridinate as solid, devolvate, and then make up suspension?

(3) Suggest suspension of unground material, separation of particle size through settling rate. Are initial small particles less active? Or through settling rate of dust or screening.

(4) Suggest use of inhibitor in oil?
(1) provide in oil are not deteriorating at normal rate — must be oxidizing salcomine.

(5) For God's sake don't call two forms isomers!!

1259994

(6) Need for better analysis — functional groups in deteriate etc. N molecules in oil?

(7) Study of deterioration rate as a function of stirring rate.

(8) Initial absorption temp — (Table I) — spot temperature confirmation

(9) Gelling phenomena? — apparently not particle size deterioration since this is normal deterioration rate? Does one ~~gets~~ get small crystals in wetting agent?

(10) Send us red suspensions (red as possible)

(11) Does one get appearance of red color in absence of air? How is it effected by temperature

1259995

(12) When does CO appear? absorption or desorption? absolute amounts?

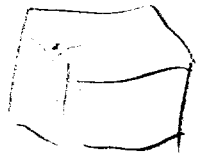
(13) Flow of inert gas cycle?

(14) Deterioration by particle size

(1) Suppose deterioration is 10A° (mean) on all sides of a cubic crystal

$V_1 = d^3$

$V_2 = (d-20)^3$



if $d = 100\,A^\circ$ $\quad \frac{V_2}{V_1} = \frac{5.12 \times 10^5}{10^6} \cong \frac{1}{2}$

$\cong 73\%$

$d = 200\,A^\circ$

$\cong 88\%$

$d = 500\,A^\circ$

$d = 1000\,A^\circ$ $\quad \frac{V_2}{V_1} \cong 94\%$

1259996

OFFICE FOR EMERGENCY MANAGEMENT

NATIONAL DEFENSE RESEARCH COMMITTEE

OF THE

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1943 Graybar Building
420 Lexington Avenue
New York, New York
October 1, 1942

Dr. Melvin Calvin
University of California
Deptarment of Chemistry
Berkeley, California

Dear Dr. Calvin:

I send you herewith a copy of the du Pont Special Report on Salcomine Deterioration. You will note that this report gives a summary of du Pont's oil suspension set-up as well as the observations which they have made upon the life of the Salcomine material in oil suspension.

There are several things of considerable interest in this report among which may be mentioned the fact that the rate of deterioration increases rapidly after about 130 hours of operation. Also the greatest deterioration is obtained in those cases resulting in the formation of the red isomer which in some way seems to be connected with the initial treatment given the Salcomine oil suspension.

We look forward to receiving your comments upon this report.

Very truly yours,

S. S. Prentiss
dsr

S. S. Prentiss
Technical Aide
Section B-7

SSP:dsr
Encl.

CONFIDENTIAL

1259997

(Standardized receipt form for use in transmitting CLASSIFIED material)

TO: Dr. Melvin Calvin

RE: Receipt of CLASSIFIED material

Original to be signed personally by the recipient and returned to sender.
Duplicate to be retained by the recipient addressed.
Triplicate retained by sender for suspense file.

I have personally received from (sender) S. S. Prentiss, (sender's address) 1945 Graybar Bldg. New York, N.Y. the CLASSIFIED documents as identified below. I assume full responsibility for the safe handling, storage, and transmittal elsewhere of these documents in accordance with existing regulations of the O.S.R.D. governing the handling of CLASSIFIED material. The CLASSIFIED material, including enclosures and attachments, is identified as follows (In identifying CLASSIFIED material avoid any reference which might cause the receipt form to become CLASSIFIED):

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*SO: signed original PC: photostat copy
CC: carbon copy TC: typed copy

_____ (Signature)
_____ (Date)

1259998

[illegible]

[illegible]

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Submitted to Division B
National Defense Research Committee
Office of Scientific Research and Development

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Report Prepared by:

C. D. Bell
E. Field

Report Approved by:

H. W. Kruse

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By N E Broderick ADO 3/18/96

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Ammonia Department
E. I. duPont de Nemours & Co., Inc.

SPECIAL REPORT ON SALCOMINE DETERIORATION

B-7-B
B-309

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Submitted to Division B
National Defense Research Committee
Office of Scientific Research and Development

This document contains information affecting the national defense of the United States within the meaning of the Espionage Act, 50 U.S.C. 31 and 32. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

Report Prepared by:

C. D. Bell
E. Field

Report Approved by:

N. W. Krase

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Deterioration of Oil Suspensions of Salcomine

Introduction

This report is concerned with data and observations bearing on the active life of Salcomine suspensions in oil when used for the production of oxygen from air. The experimental program was carried on by two groups, and for this reason it has been convenient to divide the report into two parts. The small scale laboratory work was undertaken to throw light on problems growing out of larger scale operations. The latter were primarily for the solution of engineering problems and to provide the basis for design of a full scale unit. Because the large scale work necessarily involved long, continued tests, most of the "life" data are from that source. Results from the small scale work that duplicate observations made on the larger scale have been omitted because the latter are naturally of greater practical interest. Part I deals with larger scale work, and Part II with the smaller scale data.

1260001

Part I

I. Introduction

The development of a process for the production of oxygen from air, employing a Salcomine suspension in oil, was undertaken on a semi-works scale. The objectives were to determine optimum operating conditions and to provide the basis for design of a full scale unit. Since the rate of oxygen absorption by Salcomine suspension is materially slower than that of the dry solid, efforts were concentrated upon the determination of the absorber device which would give maximum absorption rate.

On the basis of our small scale development work, a Semi-Works unit was designed and built. Operation of this unit on the scale of 50-60 cu.ft. per hour of oxygen has furnished data on the life of Salcomine in oil suspension as observed under practical operating conditions.

II. Summary

The development and operation of the suspension process utilizing continuous circulation of Salcomine suspended in white oil has shown the following facts regarding the deterioration of Salcomine.

(1) The initial capacity of Salcomine for oxygen absorption was essentially the same whether suspended in white oil or used as a dry solid.

(2) A significant decrease in capacity of the Salcomine was always found to accompany substantial particle

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size reduction regardless of the method employed to achieve such reduction and irrespective of the presence of oil during the reduction process.

(3) The useful life of a charge of Salcomine suspension under the operating conditions employed was found to be 135 to 150 hours corresponding to 240-300 cycles. This period represented approximately 75% of the total life.

(4) An accelerating rate of deterioration of the Salcomine was observed after the capacity had dropped slightly below 5.0%.

(5) Chemical analysis of the oil from used suspensions has consistently failed to reveal more than traces of oil oxidation products. Such products if formed might, of course, have been absorbed by the Salcomine.

(6) Ultimate analysis of Salcomine which had deteriorated under operating conditions indicated the loss of two carbon atoms and one hydrogen atom, as well as the gain of two oxygen atoms.

III. Semi-Works Operation Data

A. Description of Operation

The Semi-Works unit as originally designed and operated utilized a 50-gal. stirred autoclave absorber. Salcomine suspension at 20°C. was injected continuously to the bottom of the absorber. Air at 20°C. and 150#/in.^{2} was

dispersed by an 8 in. vaned disc agitator located ca. 6 in. above the bottom of the vessel and operated at 300 r.p.m. An overflow nozzle in the side of the autoclave maintained a liquid depth of 24 in. in the absorber corresponding to a 40-gal. holdup. The adiabatic temperature rise encountered in the absorber was 10°C. when operated at about 50% saturation with a fresh suspension containing 30% solids.

The suspension from the autoclave overflowed into a small separator from which the liquid was throttled into a small agitated vessel operated under 10-25 in. Hg vacuum. Here dissolved nitrogen was purged from the system. Constant liquid level was maintained in this chamber by means of a float controller which governed intermittent operation of turbine pump. The turbine pump transferred the suspension through a heater to a tower desorber. After oxygen release in the desorber, the liquid overflowed into a feed reservoir, from which it was circulated through a cooler by a small turbine pump. Finally, cooled suspension was returned to the autoclave through a refrigerated cooler by means of a piston type pump.

B. Operating Data

The initial charge of suspension for the Semi-Works unit was prepared according to a standard method evolved from small scale work. Rumford Salcomine was screened through 10-14 mesh screen and ground with white oil for 20 hours in

a 30-gal. stone-lined ball mill. This treatment was necessary to produce a suspension stable with respect to viscosity and settling. During this preparation, it was observed that the capacity of the material after milling was 3.8%, although the capacity before milling averaged 4.3%.

A summary of the operation data collected with this first charge of suspension is shown in Fig. 1. The first 110 hours of operation were carried out as a series of six-hour states at various circulation and air rates in order to obtain engineering data for design purposes. At the end of this period, the capacity of the used suspension was found to be 2.9%. Since the capacity decrease was much larger than anticipated, the remainder of the operation was carried out at constant conditions as shown in Fig. 1 in order to note the effect of capacity decrease on actual production rate. As shown in the figure, a gradually accelerating decrease in the production rate was observed. Operation was terminated after the production rate had dropped well below 50% of its initial value under the same conditions. The final capacity of the used solids was 1.0%.

At this time it was believed that two factors in the operation of the unit contributed to the observed high rate of Salcomine deterioration: (1) The air used was saturated with water at 40°C. and 150#/in.^{2} gauge. (2) The intermittent operation of the transfer pump between the

purge vessel and the desorber allowed suspension holdup in the heater to be raised to a temperature of 120° to 150°C. during the period when the pump was not operating. Accordingly, the unit was modified to dry the air with silica gel, and the pump operation was made continuous to remove the opportunity for overheating the suspension.

During the preparation of a fresh charge of suspension, the previous observation of the loss in capacity during ball milling was substantiated. To minimize this effect, the fresh charge was prepared as follows:

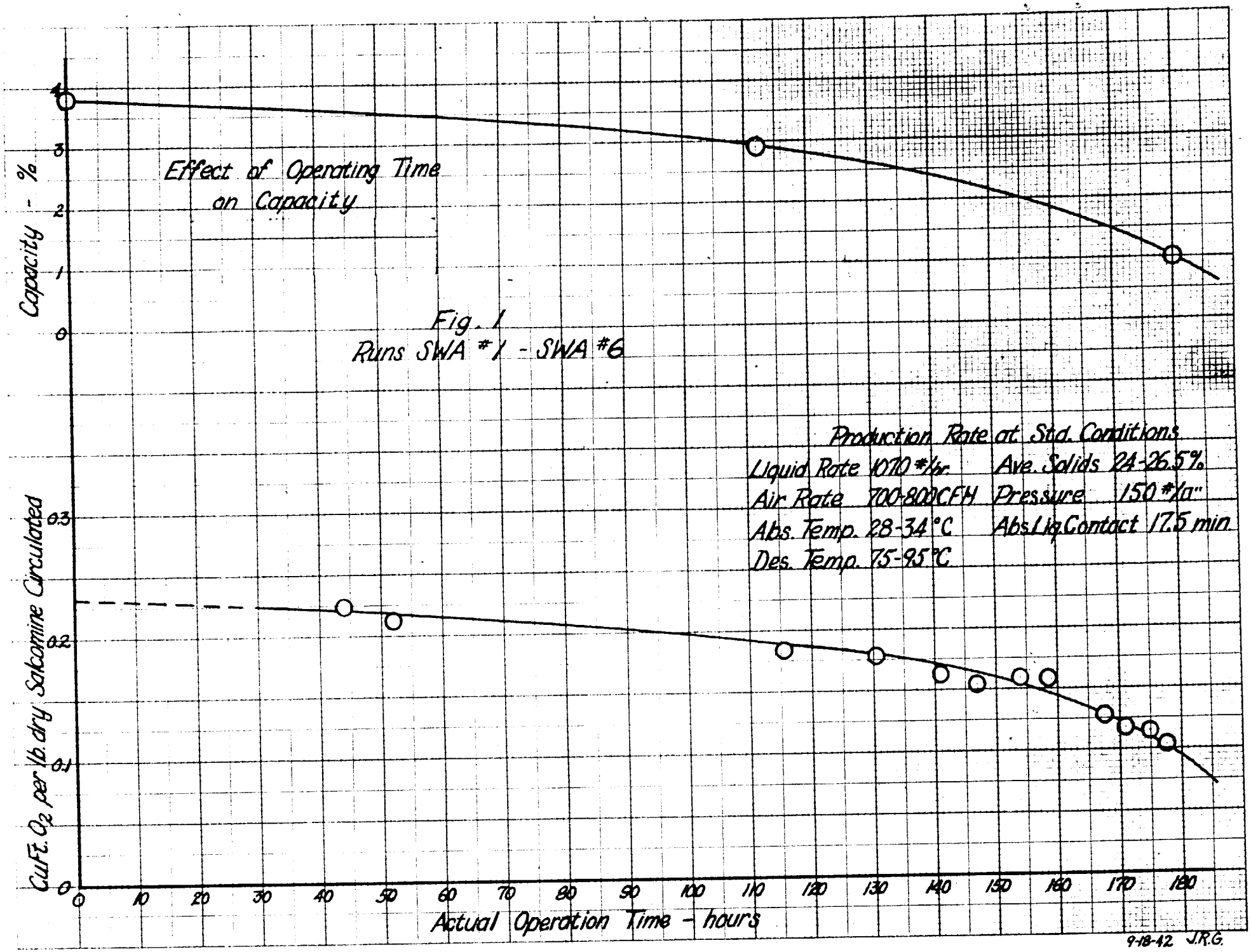
% of Total	Capacity Before Grinding	Grinding Time	Capacity After Grinding
75	4.4%	9 hrs.	4.2%
25	4.4%	20 "	3.8%
Composite	4.4%	-	4.1%

The apparatus was thoroughly cleaned before fresh material was charged.

The data observed on this material are shown in Fig. 2. By comparison with Fig. 1, it may be seen that no reduction of the salcomine deterioration rate had been achieved. In fact, the deterioration rate was somewhat more rapid, particularly near the end of the test. However, from an operating viewpoint, the useful life of the suspension was approximately the same in both tests.

C. Chemical Analyses

Several times during the course of operations,



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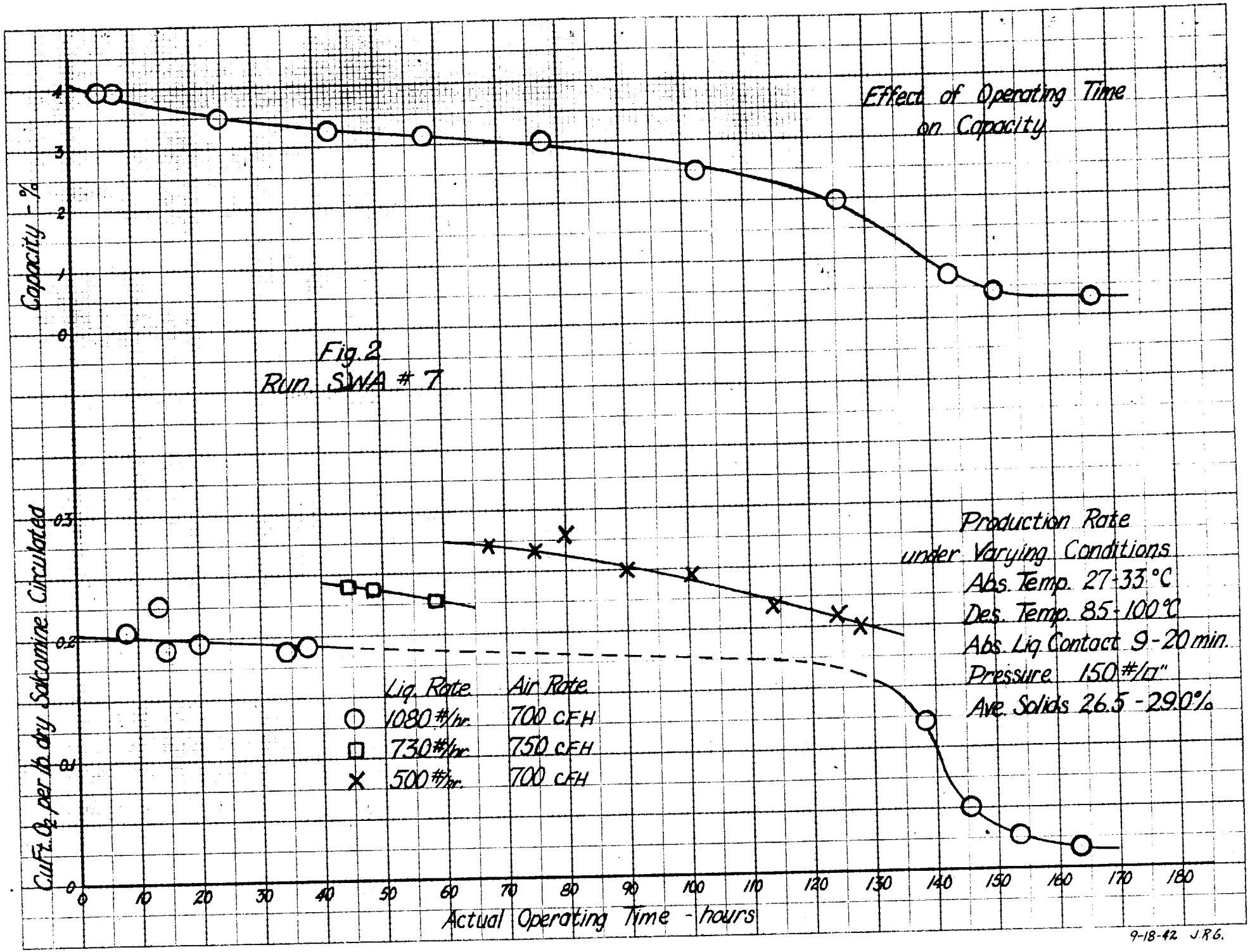
KEUFFEL & ESSER CO. N. Y.


Effect of Operating Time on Capacity
Capacity - %
Fig. 2
Run SWA # 7
Production Rate under Varying Conditions
Abs. Temp. 27-33 °C
Des. Temp. 85-100 °C
Abs. Liq Contact 9-20 min.
Pressure 150 #/□"
Ave. Solids 26.5 - 29.0%
Liq. Rate
Air Rate
1080 #/hr. 700 CFH
730 #/hr. 750 CFH
500 #/hr. 700 CFH
Cu.Ft. O2 per lb. dry Solvamine Circulated
Actual Operating Time - hours
9-18-42 J.R.G.

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one hydrogen atom as well as the gain of two oxygen atoms when compared with the empirical formula of Salcomine.

IV. Miscellaneous Experiments

A. Grinding Tests

When the suspension process was first examined, it was demonstrated that the capacity of Salcomine was the same whether the solid was suspended in oil or used dry. It was demonstrated also that Salcomine could be recovered from suspension by filtration and washing with cyclohexane, without affecting the capacity of the Salcomine.

When ball milling was first used as a means of preparing suspensions, capacity measurements showed that grinding for 20 hours at 50% solids concentration did not change the capacity of the Salcomine. However, microscopic examination showed that little size reduction was accomplished. When it was found subsequently that grinding for 20 hours at 30% solids concentration caused substantial capacity loss, two controlled grinding tests were carried out as shown below.

Grinding Time	Test I Capacity	Test II Capacity	Test II Settling Rate*
0 hrs.	4.37	4.4	12.0
1	4.41	-	-
3	-	3.9	7.0
4	4.33	-	-
6	-	4.0	5.0
7	3.81	-	-
9	-	3.8	3.0
10	3.82	-	-
13	3.82	-	-
15	-	3.5	2.5
18	3.70	-	-
20	-	3.5	1.5

* % Clear white oil observed after 14 hrs.

1260009

samples of used suspension were analysed by standard methods to determine the presence of oxidation products of white oil. The solid Salcomine was filtered off and the clear oil analyzed as follows:

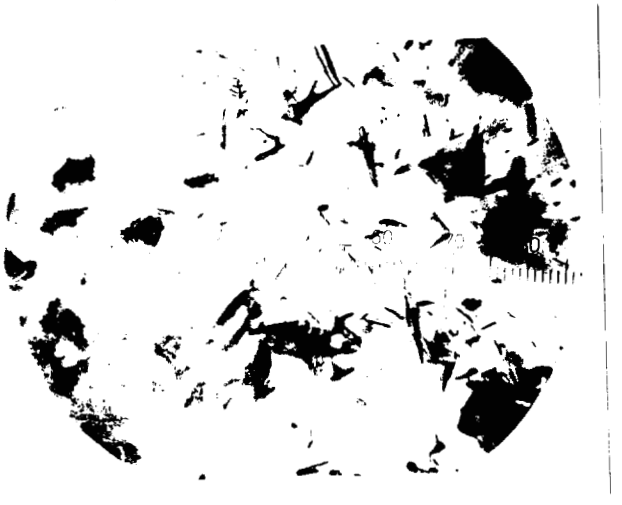
Operation Data	(Small Scale)	See Fig. 1	See Fig. 1
Time of operation	ca. 20 hrs.	110	180
Acid No.	0.007	0.013	0.0
Ester No.	-	0.00	-
Hydroxyl No.	0.000	0.00	-
Carbonyl No.	0.34	0.042	0.0
Peroxide (as H_2O_2)	-	0.00	0.002
Free Water	-	0.00	-

From these results it may be seen that no more than traces of oil oxidation products were found in any oil sample. Such products could have been absorbed by the Salcomine.

An ultimate analysis was made on the deteriorated Salcomine after SWA-5 (see Fig. 1). The Salcomine was recovered from the oil by filtration and washed on the filter with cyclohexane. The recovered solids were dried for 18 hrs. at 60°C. in an open oven. The results of the analysis are shown below.

Element	Av. Wt. %	Atoms/Atom of Cobalt
Cobalt	17.88	1.0
Carbon	50.22	13.8
Hydrogen	3.89	12.7
Nitrogen	7.32	1.72
Oxygen (by difference)	20.69	4.26

These results indicated the loss of two carbon atoms and



A

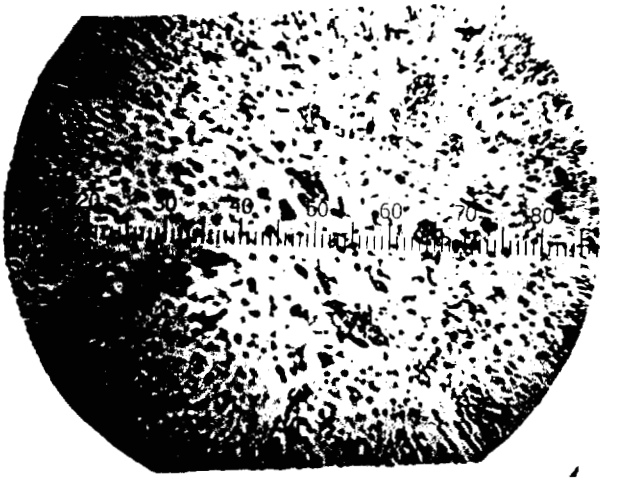
Unground Salcomine
Cap. = 4.4%

B

Ball Milled 9 hrs. at
30% solids conc.
Cap. = 3.8%

C

Ball Milled 20 hrs. at
30% solids conc.
Cap. = 3.[illegible]%



D

Deteriorated Salcomine
suspension
Cap. = 1.0%

Fig. 3 - 1700x Photomicrographs of Salcomine Suspensions.

<u>Note</u>: 1 division on the scale in the pictures equals 1 micron.

Test I was carried out in a small steel mill with steel balls, while Test II was made in the 30-gal. stone mill with flint pebbles. In Fig. 3 are shown photomicrographs of samples from Test II. Data on measurement of settling rates agreed well with the photomicrographic evidence that the reduction in Salcomine capacity was a function of particle size reduction.

A few miscellaneous methods of grinding were tested to determine whether the presence of white oil during grinding was connected with the capacity loss. These are listed below.

Apparatus Tested	Salcomine Capacity Original	Salcomine Capacity After Grinding
Hand Mortar	4.4	4.1
Mikropulverizer	4.4	2.8
Ball Mill	4.4	Caked; No grinding.

Since these tests showed capacity loss wherever size reduction was accomplished in the absence of white oil, it seemed apparent that the physical presence of white oil during the operation had no effect upon capacity loss.

1260012

Part II

I. Small Scale Tests Involving Deterioration of Salcomine Suspension

A series of simplified life tests on 25% Salcomine suspensions in White Oil was carried out in which oxygen continuously passed through the suspension while alternately heating to 90-95°C. for 5 minutes and cooling to 30°C. for 25 minutes. The normal cycle is from complete desorption to 60% of saturation. Except for Life Test A (See Table I) the heat transfer was by means of an external jacket. An electrically driven stirrer was provided. Cylinder oxygen was dried by passing over soda-lime and KOH pellets at 100 lb. pressure. Samples of suspension were taken at regular intervals, centrifuged, washed with cyclohexane, dried and then examined by our standard procedure for the dry solid.

Results to date are summarized in Table I. Life Test A shows a degradation rate of only 3% per 100 cycles for the first 300 cycles, which then increases rapidly to 15% in the period of 500 to 850 cycles. A comparison with Life Test D suggests that the initial excellent performance is the result of low absorption temperatures. The subsequent more rapid degradation may be ascribed to excessive water introduced by the sweating of the cooling coil during a period of very humid weather. The possibility still remains, however, that optimum traces of water were present in the early part of the test.

Table I

Summary of Laboratory Life Tests

Test	Cycle	Suspension	Oxygen	Abs. T	% Cap.	Degrad. %? 100 Cycles	Remarks
A	0	20 hr. milled	Cylinder	15°C.	3.8%	-	Open coils for cooling caused H_2O condensatio
	300	"	"	"	3.5	3%	
	500	"	"	"	2.9	-	
	850	"	"	"	1.2	15	
D	0	"	Dry O_2	30°C.	4.0	-	
	200	"	"	"	3.1	11	
	500	"	"	"	1.3	13	
C	0	"	O_2 sat. at 25°C.	30°C.	4.0	-	
	100	"	"	"	2.8	30	
	290	"	"	"	1.4	22	488 g. H_2O through 350 g. Salcomin
H	0	Unmilled; dispersed in unit	Dry O_2	30°C.	4.4	-	
	100		"	"	4.0	-	
	245		"	"	3.2	11	Set up to thick gel
G	0	Unmilled plus 1% "Duponol" G	Dry O_2	30°C.	4.2	-	"Duponol" reacts. Thickens but does not set up.
	100		"	"	3.7	12	
	340		"	"	2.4	13	
J	0	Unmilled; dispersed in Waring Blendor	Dry O_2	30°C.	4.4	-	
	50		"	"	4.1	14	Very rapid drop. Red color indicates isomerization.
	180		"	"	0.31	66	

1260014

The harmful effect of large amounts of water is shown in Life Test C where double the degradation rate with dried O_2 was obtained by saturating the O_2 with water at 25°C. A test of the effect of traces (0.1 mm. partial pressure) of water is in progress. The value of low temperature operation has not yet been checked.

The above life tests were performed on Salcomine ball milled in White Oil, since this milling appears necessary for operation of the semi-works unit. A series of tests was performed to determine whether milling affects life. In Test H unmilled material was suspended by an ordinary stirrer. Degradation proceeded at the same rate as for the milled Salcomine (starting at a higher level because the milling loss was not introduced) but after 245 cycles the suspension had formed a thick, non-pouring gel. Microscopic examination revealed the presence of extremely minute crystals. Setting-up of the gel is prevented by the addition of "Duponol" G, an oil soluble wetting agent, but the rate of deterioration is still the same. A suspension prepared by high speed agitation in a Waring Blendor shows a very rapid loss in capacity also without gelling (Test J). The recovered solid took on the red color of the inert red isomer of Salcomine.

A batch of Salcomine ball milled for 20 hours as a 39% suspension underwent no apparent change in particle size

and no loss in capacity. The high concentration appears sufficiently viscous to reduce the effect of the mill. A change analogous to that produced by the Waring Blendor appears to have taken place, however, since a life test now in progress on this material showed rapid degradation with formation of the red color, and no thickening during operation. One might postulate that in both cases a polishing of the crystals occurred which eliminated the gelling action. It is more difficult, however, to explain the formation of the red color. We need to know more about the mechanism of formation of the inert red isomer.

A stability test on the above suspension was carried out by passing oxygen through slowly at 100°C. (no cycles). After 106 hours the recovered Salcomine was red in color and almost completely inert. This result is contrary to an early test in which an unmilled 10% Salcomine suspension was treated at 98° for 150 hours (except for 21 cooling cycles to measure capacity) in which a loss in capacity of only 5% was observed. Tests at other temperatures are in progress. A Salcomine suspension subjected to 200 cycles between 30° and 95° in our life test unit with no oxygen flow suffered no deterioration.

White Oil is slowly oxidized by pure O_2 at 100°C. Salcomine, however, appears to effectively inhibit the oxidation of White Oil: thus White Oil plus 0.5% Salcomine contained no trace of aldehyde, ketone, acid or peroxide after exposure to oxygen for 148 hours at 100°C.

1260016

The oxygen produced by the semi-works unit was found to contain 0.004-.006% CO when operating at 25-30°C. absorption, 85-95°C. desorption, 150 lb. air pressure. In one test at 45°C. absorption the CO had risen to 0.026%. If the amount of CO is related to the rate of oxidation of Salcomine, it appears that higher absorption temperatures accelerate this reaction.

Based on our experience to date we can summarize the factors involved in the life of a Salcomine suspension as follows:

1. Oxidation of the Salcomine itself appears to be a primary cause of degradation. This is based on ultimate analysis of semi-works spent Salcomine, the presence of CO in off-gas, and the observed adverse effect of increased absorption temperatures.

2. Excessive water in the oxygen accelerates degradation (steam will hydrolyze Salcomine). The effect of water in traces is yet to be determined.

3. Most rapid degradation has occurred when a red color has been observed in the recovered solid, which may indicate formation of the inert red isomer. Until the variables that influence transformation from one isomer to another are understood and controlled, it is reasonable to expect non-reproducible results in life tests.

1260017

stupid!

4. As far as we know, the oxidizability of White Oil has not contributed to the degradation of Salcomine.

5. A temperature cycle in the absence of oxygen does not appear to degrade Salcomine.

1260018

Appendix

1260019

Appendix A

I. Specifications of No. 30 White Oil (Supplied by L. L. Sonnenborn Sons, 88 Lexington Ave., N. Y.)

A.P.I. Gravity at 60°F.	49-51
Sp. Gr. at 60°F.	0.775-0.878
Saybolt Viscosity at 100°F.	30-35
Flash Point °F. Open Cup	170-180
Flash Point °F. Closed Cup	135-145
Initial Boiling Point	380°F. or 193°C.
Distillation End Point	490°F. or 254°C.
USP Acid Test	Passes
Unsulfonatable Residue	97% or higher
Fire Point	-25°F.

No. 30 White Oil is a hydrocarbon oil from which all aromatic hydrocarbons as well as unsaturated naphthenes and paraffins have been removed. White Oil is predominantly saturated aliphatics with traces of saturated naphthenic constituents. The average formula may be written C_nH_{2n} where n = 10-12. The average molecular weight = 154.

1260020