INVESTIGATION OF OXYGEN PRODUCTION BY METAL CHELATES

BY R. F. STEWART, P. A. ESTEP, AND J. J. S. SEBASTIAN

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INVESTIGATION OF OXYGEN PRODUCTION BY METAL CHELATES[1]

by

R. F. Stewart,[2] P. A. Estep,[3] and J. J. S. Sebastian[4]

SUMMARY AND CONCLUSIONS

A key step in changing coals to fluid fuels and chemicals is the conversion of coal to synthesis gas by gasification with steam and oxygen. As oxygen represents one of the largest single expenses in gasification, its cost is a vital factor in the economy of the process. At present, the most economical method for producing tonnage oxygen is by the conventional rectification of liquefied air. Several alternate methods have been proposed for producing oxygen from air: (1) methods based on physical or chemical sorption of oxygen from air by liquids or solids or (2) the oxidation of certain inorganic compounds to higher oxides unstable at higher temperature levels. Economic limitations are discussed by which these methods may be evaluated.

Chelated metals of the salcomine type are promising chemical sorbents of oxygen from air. This report covers a study of the reversible sorption of oxygen by salcomine and other chelates. The presence of water in the salcomine structure was verified; it is the loss of this water that causes slow deterioration of salcomine during cycling.

The metal chelate process is not economical at this time for producing tonnage oxygen required in coal gasification. However, the salcomine process may possibly be used in small-scale production of oxygen, such as for welding on shipboard, where cost is not a primary consideration. The most favorable conditions for such applications are discussed. A bibliography of abstracted references on the production of oxygen by chemical processes is included in this report.

INTRODUCTION

The object of this project was to explore the possibility of developing a process for producing tonnage oxygen by a method other than conventional

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rectification of liquefied air. The oxygen was to be used for gasifying coal with steam under pressure. If the operating cost for the production of oxygen, \$5-\$6 per ton in a 500-ton-per-day conventional plant (75),[5] could be lowered, the cost of liquid fuels from coal would be affected to a considerable extent. Also, availability of low-cost tonnage oxygen might aid the steel industry by permitting an increase in output from existing blast furnaces, open hearths, and similar equipment.

Several methods have been proposed from time to time for producing oxygen from air. Some involved physical, others chemical sorption of oxygen by liquids or solids, and some were based on the oxidation of inorganic compounds to higher oxides. In all instances oxygen was to be recovered by desorption or by a reversal of reaction (reduction) brought about by steam stripping, increase of temperature, or decrease of pressure. None of the proposed methods has been developed to commercial production.

Among the chemical sorbents proposed as oxygen carriers, the chelated metals of the salcomine type appeared to be the most promising.

Salcomine, a coordinate covalent compound of cobalt with 1 mole of ethylenediamine and 2 moles of salicylaldehyde, in which cobalt forms the center of three organic rings, had been tested as oxygen sorbent by the U. S. Navy during World War II (44). Oxygen was produced aboard a destroyer tender for several months in rather crude equipment with the granular absorbent packed into three holders. In spite of unfavorable conditions, oxygen was produced at a cost not exceeding that of cylinder oxygen and was utilized for welding and cutting operations. However, its use was discontinued because of the wartime shortage of cobalt and the limited life of the sorbent. Thirteen declassified National Defense Research Council reports[6] on the development of oxygen-carrying chelates by various investigators at the University of California, Iowa State College, Massachusetts Institute of Technology, University of Pennsylvania; E. I. du Pont de Nemours & Co., Rockefeller Institute, Rumford Chemical Works, and Arthur D. Little, Inc. and a number of publications by Melvin Calvin and associates, Harvey Diehl, T. A. Geissman, Benjamin B. Fogler, and others, describe most of the work which was done during World War II to produce oxygen by chemical means.

Bureau correspondence with those who developed the chemistry of chelates under the broad program sponsored by the National Defense Research Committee indicated that some of the investigations have been continued beyond the wartime program. Calvin stated that fluorine and certain alkoxy derivatives of cobalt salcomine have a greatly increased life and utility for oxygen production. Geissman referred to more recently developed methods of sorption and felt that the process has possibilities that should be investigated.

The establishment of certain economical limitations (listed under Process Economics) indicated that a process based on the production of oxygen by reversible sorption offered promising economic possibilities.

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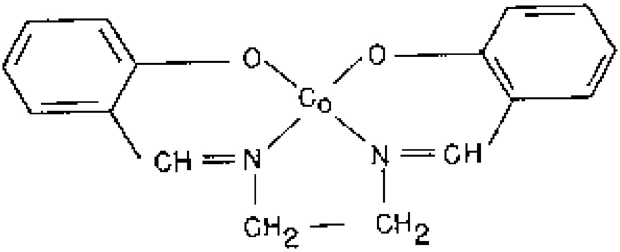
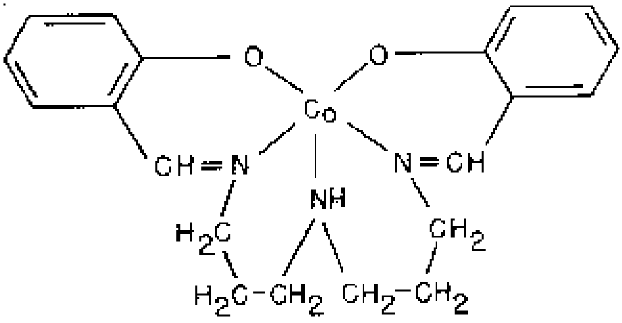
[5] Underlined numbers in parentheses refer to items in the Bibliography at the end of this report.

[6] See introduction to Bibliography.

Only a few coordination compounds can combine reversibly with molecular oxygen without any structural change (77). Among these few are the metal-porphyrin-protein complexes, such metal chelates as hemoglobin and hemocyanin, which transport oxygen in living organisms. All of them being proteins, investigation of their sorption properties is difficult, due to their complicated structure. The development of synthetic oxygen-carrying coordination compounds is recent; thus far, only certain chelates of cobalt have been found promising, yet a relatively large number of cobalt chelates (14, 101), both in solution (56) and in the solid state (3, 64), have been reported capable of reversible reaction with oxygen.



TYPE I



TYPE II

FIGURE 1. - General Types of Cobalt Chelates.

Figure 1 shows two general types of bis-salicylaldehyde imine-cobalt chelates acting as reversible oxygen carriers. Type I, bis-salicylaldehyde ethylenediimine-cobalt, is commonly called salcomine and abbreviated Co-Sal-en; type II is bis-salicylaldehyde-3,3'diimino-di-n-propylamine cobalt. In general, compounds of type I can absorb 1 molecule of oxygen per 2 atoms of cobalt, those of type II absorb 1 molecule of oxygen for each atom of cobalt. These two structural types appear to be the only chelates that offer economic possibilities for producing oxygen.

Work on these types of compounds during World War II emphasized practical results. Little fundamental research was carried out, and much of the information has not been correlated. Following the war, more fundamental work was reported, principally by Diehl and coworkers. Virtually no chemical methods of oxygen production have been investigated during the past few years.

Although a salcomine process had been developed for naval use so that it could be operated with any inlet-air pressure, for convenience it was operated with 90-100 p.s.i.g. air, which greatly increased the cost. As another example, among several hundred salcomine derivatives investigated, some showed considerably better properties than the parent compound. However, in none of the published reports was the additional cost of synthesis considered in the overall cost of producing oxygen.

This report describes a limited amount of experimental work to (1) determine optimum economic conditions for some technically feasible processes, (2) resolve conflicting reports regarding optimum process conditions, and (3) test new compounds.

APPARATUS, EXPERIMENTAL PROCEDURE, AND RESULTS

Several types of apparatus were used or developed for the experimental work. A polarograph and a small glass apparatus were used for rapid screening of metal chelates for their activity in reversible sorption of oxygen. Special apparatus was constructed for cycling in solution and suspension, for qualitative and quantitative investigation of deterioration, for specific recovery, and for analytical determinations.

A Sargent Model XXI polarograph was used to test the ease of reduction and the reversibility of oxygenation of commercial chelates, mainly versenes, which had never before been tested for their capabilities for reversible sorption of oxygen. A solvent was chosen on the basis of the solubility of the chelate, but with full consideration of the dielectric constant and electrolytic properties of the solvent. Half-wave reduction potentials for the unoxygenated and oxygenated chelate were then determined. Reversibility of the reaction at the dropping mercury electrode (d.e.) was indicated by a slope of 0.059 (45) for the plot of $E_{d.e.}$ as a function of the log of $i/(i_d-i)$; i_d is the limiting value of the diffusion current, and i is the diffusion current when the potential of the dropping electrode is $E_{d.e.}$

Another test of reversibility is based on the constancy of the half-wave potential with variation in the concentration of the solution tested. The half-wave potential is independent of concentration, if an ion is reversibly reduced. For the irreversible reduction of an ion to a lower valent or molecular state, the half-wave potential usually becomes more positive with increased concentration (40).

Half-wave potentials obtained for the reduction of absorbed or bound oxygen from typical solutions are shown in Table 1.

TABLE 1. - Half-wave reduction potentials for oxygen in the presence of versene-type[1] metal chelates

	First wave (reduction of O_2)	Second wave (reduction of H_2O_2)
Oxygen in solution....................	-0.250	-1.080
Cupric disodium versenate + O_2.........	- .253	-1.040
Manganous disodium versenate + O_2.....	- .330	-1.230
Cobaltous disodium versenate + O_2.....	- .297	-1.185
Nickelous disodium versenate + O_2.....	- .300	-1.186
Ferma-Kleer Iron (iron versenate) + O_2	- .300	-1.060

[1] Polyamino-polycarboxylic acids (usually polyamino-polyacetic acids) are used as complexing or chelating agents.

In the presence of these chelates oxygen has a more negative half-wave reduction potential than in their absence. According to Feber (40), this indicates more difficult reduction of oxygen and thus shows poor sorption and carrying characteristics. Oxygen carriers should show less negative half-wave potential. For example, salcomine caused the half-wave potential for the reduction of dissolved oxygen to shift from -0.48 to 0.28, indicating a greater ease of reduction (or sorption) of oxygen, which is characteristic of a good oxygen carrier.

To verify certain results of polarographic screening and to test compounds which are only available in small quantities, a simple glass apparatus was assembled (see fig. 2). This apparatus permitted testing of promising compounds within an experimental error of 5 percent under widely varied conditions of temperature and pressure. The general testing procedure was as follows:

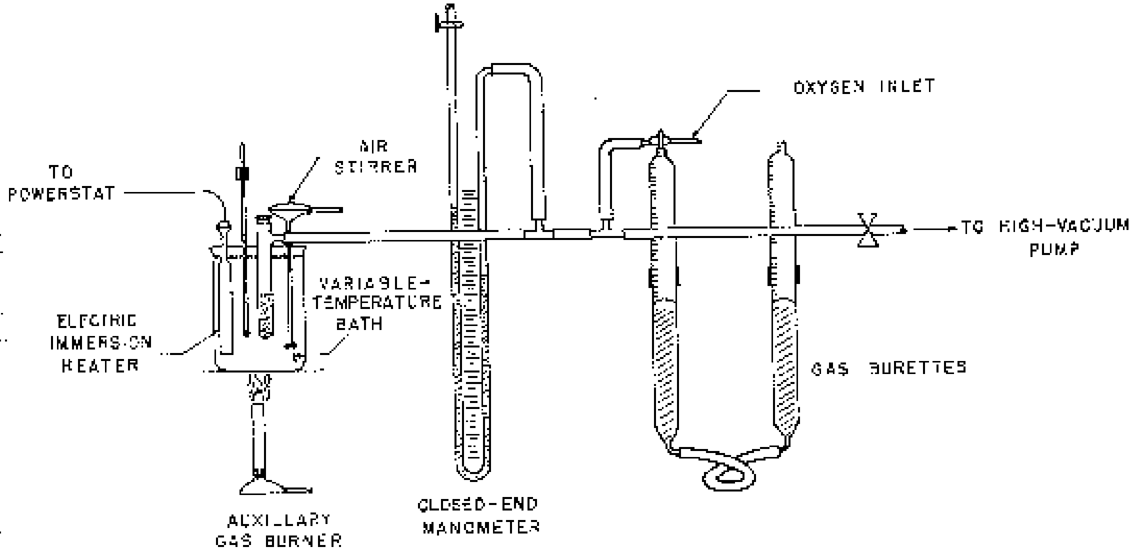


FIGURE 2. - Glass Apparatus for Preliminary Oxygen Sorption-Desorption Tests.

A 5-gram sample of chelate was placed in a stoppered side-arm test-tube and was immersed in a bath of glycerin agitated by means of an air stirrer. During desorption the bath was heated electrically at a predetermined rate. A closed-end mercury manometer indicated the pressure in the system. Pure cylinder oxygen was measured and introduced by a calibrated gas burette filled with mercury, with another burette of the same size used a leveling bulb. A high-vacuum pump reduced the pressure during activation of the sorbent and before sorption of oxygen. All connections were sealed with wax to make the system leakproof.

The chemical compounds tabulated below have been tested, either by polarographic methods or in the glass apparatus shown in figure 2, without any evidence of reversible oxygen sorption:

Barium disodium versenate.
Cupric disodium versenate.
Cobaltous disodium versenate.
Disodium calcium versenate.
Lead disodium versenate.
Magnesium disodium versenate.
Manganous disodium versenate.
Nickelous disodium versenate.
Strontium disodium versenate.
Zinc disodium versenate.
Perma-kleer iron (an iron versenate).

Typical curves for oxygen sorption and desorption by salcomine are shown in figures 3 and 4. Salcomine steadily removes oxygen from air at a rate proportional to the pressure above the sorbent and the removal of the heat of sorption from the system. Oxygen is then released by heating the granular salcomine to 80°-90° C. The time required for oxygen sorption is a highly essential variable from the standpoint of process economics. It determines equipment and plant size, which are reflected in the ultimate cost of tonnage oxygen. The time required for oxygen sorption depends upon a number of interrelated factors, such as synthesis procedure, size of salcomine granules, procedure for activation, partial pressure of oxygen, and temperature of the sorbent.

Salcomine can be synthesized by several methods. Considerable care must be used in the preparation to produce this sorbent in its most active physical state, in order to approach its theoretical oxygen-carrying capacity. The factors involved in the preparation have been well described by Diehl (32). Even under apparently identical conditions, there is considerable lot variation in small-scale batch synthesis. For example, two lots of salcomine prepared by Diehl's method A required 110 and 128 minutes, respectively, to reach 95-percent oxygen saturation. The particle size of the granular salcomine also affects the rate of oxygenation. Fine crystals from the second filtration of one of the above lots were found to be more active, reaching 95-percent saturation in only 80 minutes. Variations in sorption time as high as 100 percent can be expected for different lots of salcomine.

Following preparation, salcomine must be activated to remove the chemically bound solvent and permit reversible oxygen sorption. Salcomine is activated by heating to 130° C. under reduced pressure of less than 1 mm. Hg (abs.) for at least 1 hour. Table 2 gives the effect of variation in activation conditions on the time required for salcomine to reach 95-percent oxygen saturation. No increase in sorption time has been obtained by activation at temperatures above 130° C. under reduced pressure. An increased amount of deterioration occurred at higher temperatures.

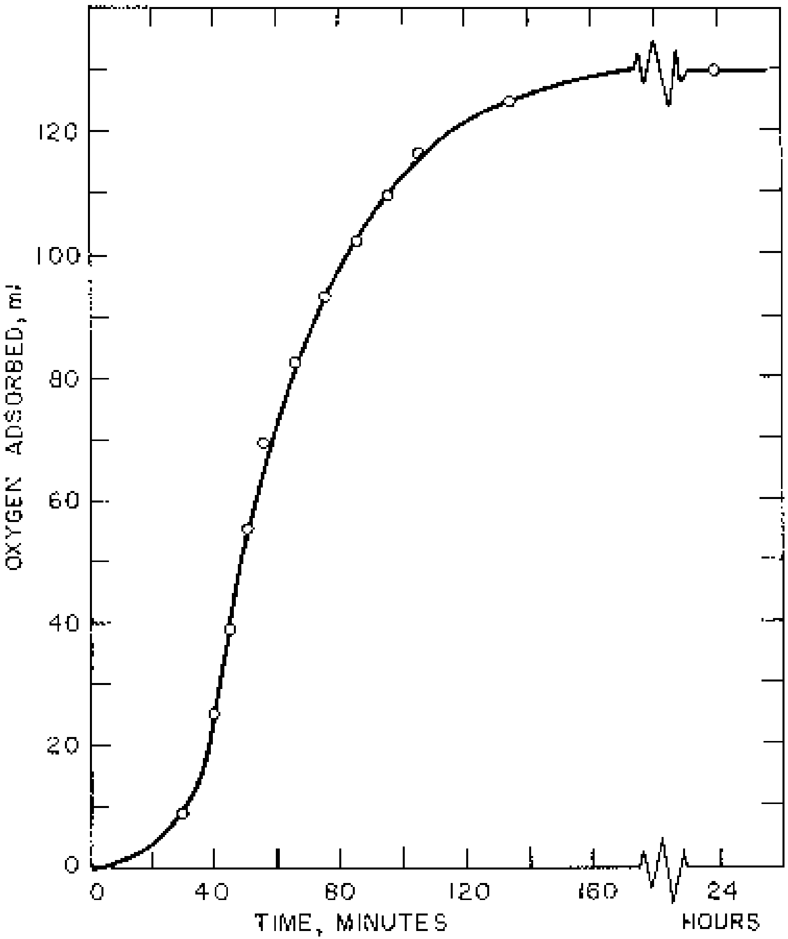


FIGURE 3. - Oxygen Sorption in Glass Apparatus at 25° C. and Atmospheric Pressure Test No. 2–Sorbent: Salcomine, 5 Grams.

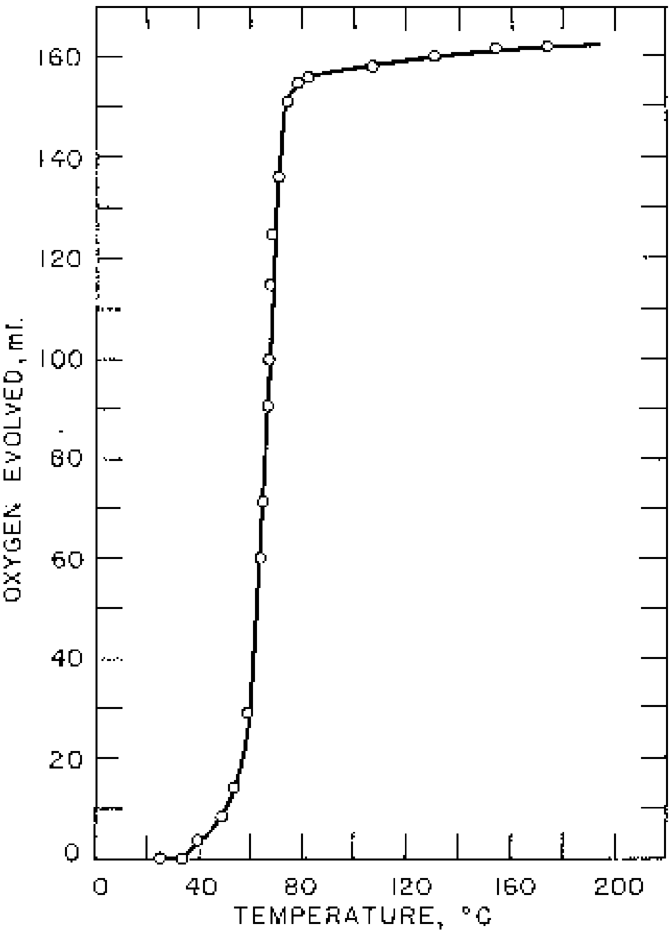


FIGURE 4. - Desorption of Oxygen in Glass Apparatus at Atmospheric Pressure Test No. 8–Sorbent: Salcomine, 6 Grams.

TABLE 2. - Effect of activation conditions on oxygenation of salcomine

Temp., ° C.	Pressure	Duration, hours	Sorption time, minutes
110	Reduced	1	240
130	do.	1	145
180	do.	4	145
130	Atmospheric	12	Inactive.
180	do.	12	Slight.

The effect of oxygen pressure is shown in Table 3. The results show that the time required to reach 95-percent oxygen saturation decreases with increase in air pressure, but the cost of air compression also increases (see Process Economics). The optimum economic pressure is as little above atmospheric as is necessary to overcome the pressure drop across the sorbent bed.

TABLE 3. - Effect of oxygen pressure on oxygenation of salcomine

Partial pressure of oxygen, mm. Hg	Total pressure of air, p.s.i.a.	Sorption time, minutes
144	13.3	155
160	14.4 (from fig. 3)	145
240	22	120
745	14.4 (pure oxygen)	90

Table 4 shows the effect of the temperature of salcomine on the time required to reach 95-percent oxygen saturation.

TABLE 4. - Effect of temperature of salcomine on sorption time

Temperature, ° C.	Sorption time, minutes
35	160
25	145
15	110
10	96
0	80
-10	85
-18	105

The rate of oxygenation is seen to decrease at either higher or lower temperatures; the optimum is approximately 0° C. However, the temperatures measured are estimated to be within 10°, owing to inaccuracies caused by the heat produced during sorption. Both bulb-type mercury thermometers and thermocouples placed in the granular salcomine bed showed a temperature that is probably between those of the flowing air and the slowly heating salcomine particles. It is apperent, however, that the optimum temperature of oxygenation is 0° to 10° C. or slightly higher. A similar optimum temperature of about 15° C. has been reported (30), with little difference in saturation time between 5° and 25° C.

Since the rate of oxygenation of granular salcomine is strongly dependent on oxygen pressure and on the rate of diffusion of oxygen to the salcomine, the velocity of air through a packed bed or a fluidized column greatly affects the sorption time. Table 5 gives a comparison of the results obtained in static and in flowing air under several conditions. The apparatus was the same as shown in figure 2, consisting of a vertical tube with an air inlet at the lower end to retain a packed bed of salcomine. Comparison of tests with approximately the same amount of air, shown in items 1 and 2, indicated a large increase in the rate of oxygenation when air was moved through the salcomine bed. If the air-flow rate is increased until not quite all of the oxygen is absorbed, as in item 3, the time required to reach 95-percent saturation is only 10 minutes.

TABLE 5. - Effect of air velocity through granular salcomine

Item	Flow conditions at 20° C. and atmospheric pressure	Sorption time, minutes
1....	Static air	145
2....	Flowing air, with 99% O_2 removal	23
3....	Flowing air, with 96% O_2 removal	10
4....	Flowing oxygen (equivalent to air at 70 p.s.i.a.).	4.5
5....	Flowing air through packed bed at 80 to 90 p.s.i.a. pressure, above 25° C., from reference (44)	6 to 8
6....	Flowing air through fluidized column of salcomine at 5 std. cu. ft. per hour, with 4- to 5-percent oxygen removal.	6 to 8
7....	Same as item 6 at 15 std. cu. ft./hr.	7.2

Less than 5 minutes was required for saturation in the test shown in item 4; although pure oxygen was sorbed in this test at atmospheric pressure, the effect would have been the same as if air at 70 p.s.i.a. had been employed (the partial pressure of oxygen in the latter case being 14.7 p.s.i.a.). In this instance the oxygenation rate depends largely on the rate of heat removal from the salcomine bed.

For comparative purposes, sorption data from a large shipboard unit having operated under similar conditions are included in item 5. In items 6 and 7 fluidized columns of salcomine were tested in a large excess of air, which itself provides the cooling medium for the fluidized salcomine. A significant decrease in sorption time was obtained compared with item 3. Probably the uniform cooling would decrease salcomine deterioration, but the compression cost of the large excess of air would be prohibitive in commercial application.

One effect, group substitution in salcomine, was not investigated experimentally but is included here for comparison. Of hundreds of derivatives that have been synthesized, a few have properties superior to the parent compound. Typical results are shown in table 6. The rate of oxygenation of certain of these derivatives of salcomine, particularly the 3-nitro derivative, is faster than that of salcomine under the same conditions; but the cost of any of these derivatives is much higher than that of the parent compound. For example, the nitration of salicylaldehyde in the synthesis of 3-nitro salcomine is estimated to increase the cost of the sorbent from $2.25 to $10-$20 per pound. With some compounds, such as the 3-fluoro derivative, deterioration of sorbent is reported to be considerably less than that of salcomine, but accurate measurements of the rate of deterioration have not been reported.

TABLE 6. - Effect of group substitution in salcomine on sorption time

Item	Derivative and testing conditions	Sorption time, minutes
1....	3-nitro salcomine, at 26° C. Sorption from flowing wet oxygen at atmospheric pressure to 50% saturation; from reference (55) - compare with item 4, table 5.	1 to 2
2....	3-methoxy salcomine, at 0° C. Sorption from flowing air at atmospheric pressure to 88% saturation; from reference (31).	7
3....	3-ethoxy salcomine, at 20° C. Sorption from flowing air at atmospheric pressure to 50% saturation; from reference (32).	13
4....	3-fluoro salcomine at 25° C. Sorption from flowing oxygen at 150 mm. Hg. pressure to 95% saturation; from reference (3).	9

An evaluation of these results, compared with conclusions published by Diehl, Calvin, Fogler, Geissman, and others, permitted the establishment of tentative optimum economic conditions for using chelates:

(1) Salcomine itself, rather than one of its many derivatives, should be used, as improvements in operating conditions are not compensated for by the greatly increased cost of synthesizing derivatives.

(2) Salcomine should be synthesized by direct mixing of reactants, according to method A of Diehl (28), to produce "fine-grained" material of granular size.

(3) An absorption temperature of 20° to 25° C. should be used. Lower temperatures increase the rate of oxygen sorption but also consideraly increase the operating costs.

(4) Air at 1.1 p.s.i.g. should be used during sorption, which should be sufficient to compensate for pressure losses across the sorbent bed and connections. Higher pressures increase the rate of oxygen sorption but also increase compression costs (see Process Economics).

Cycling in Solution

An obvious approach to prevent deterioration was the cycling of salcomine in solution. Another reason for this approach was that, from an engineering standpoint, problems of heat transfer are greatly lessened in solution.

furthermore, local overheating, which increases deterioration, would be considerably reduced.

Various workers (11, 14, 56, 77) in this field have reported that salcomine-type chelates can react reversibly with oxygen in solution. In most instances, however, the chelate became inactive after a few cycles, yet, in certain cases (56) a high percentage of activity has been reported for the second and third cycles. No attempt has been made to cycle further. Calvin and his associates (14) reported that a large number of cobalt compounds absorb oxygen when dissolved in nonaqueous solvents, but all lost activity after a few cycles. They prepared certain types of cobalt chelates which were water soluble and succeeded in cycling them as many as 20 times, with less than 5-percent deterioration. Unfortunately, the work had been terminated before definite conclusions could be reached, and no further details have been published.

Figure 5 is a sketch of the glass apparatus for continuous cycling of sorbents in solution. The solution (for example, salcomine dissolved in xylene) was cycled countercurrently to air. Oxygen was to be absorbed from the air by the cold solution. The solution was then to be heated and the

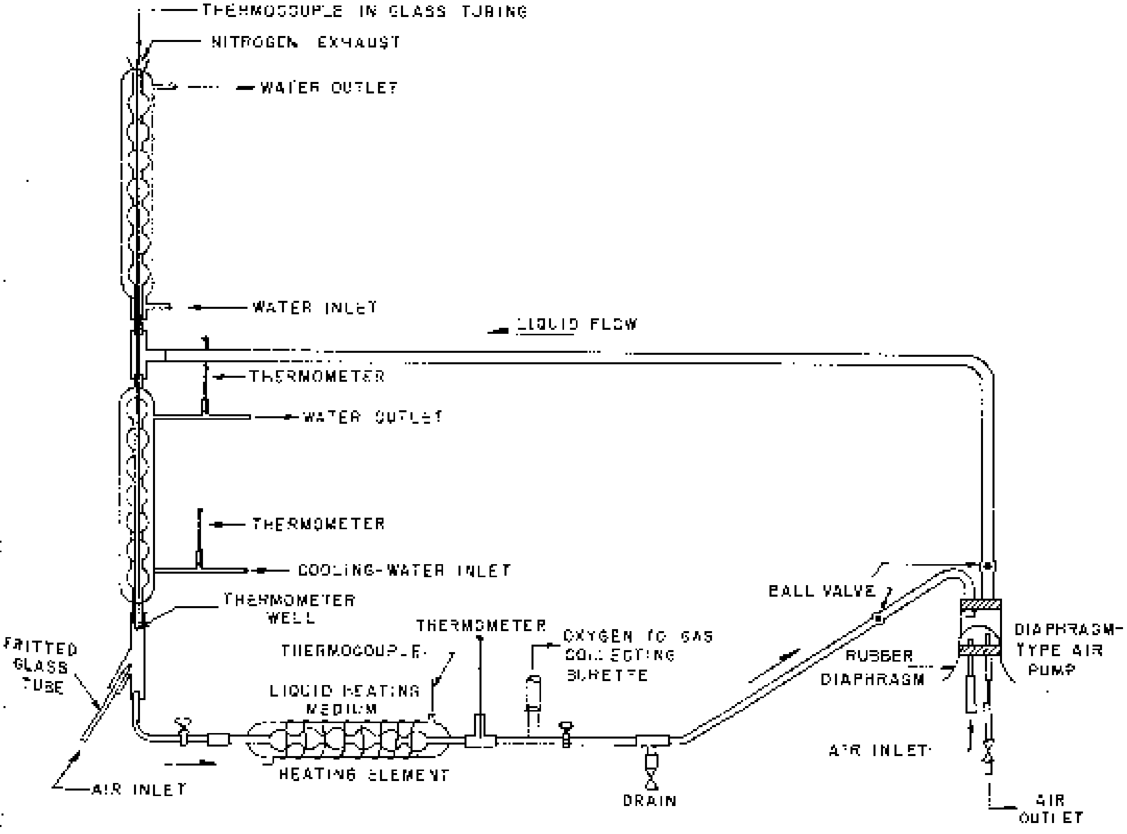


FIGURE 5. - Glass Apparatus for Continuous Cycling of Oxygen Sorbents in Solution.

desorbed oxygen collected and measured. With a pure solution of salcomine in xylene or pyridine, no oxygen was produced. However, when the solution contained suspended salcomine (normally the case because of the low solubility of salcomine), oxygen was initially produced in proportion to the amount of suspended solid.

In all instances in which a mixture of salcomine in either xylene or pyridine was first filtered to remove undissolved particles of salcomine, no oxygen was produced. Whenever the cycled solution contained suspended salcomine, a small amount of oxygen was collected initially, but the sorption and desorption soon stopped. Salcomine mixed with xylene formed a black, viscous suspension; the suspended particles did not settle and were removed only by filtration. Initially a true solution of salcomine in xylene did take up a small amount of oxygen, but the sorption was apparently an irreversible oxidation, since the solution desorbed no gas below the boiling point of the solvent.

Salcomine is only very slightly soluble in organic solvents, although its solubility is somewhat better in polar solvents, such as pyridine. But in all these solvents, the "open bond" (in position I, see below) attracts solvent molecules and prevents reversible oxygen sorption after the first few cycles. Even with less polar solvents, such as benzene or xylene, a solvent molecule is apparently preferentially sorbed in place of oxygen, and the chelate becomes inactive to further oxygen sorption after a few cycles, according to the present interpretation of the mechanism of sorption. It is believed that all reported cases of reversible sorption in solution are due to absorption by sorbents suspended in saturated solutions.

Another possibility is cycling of salcomine suspended in oils or other inert fluids. Considerable work on this method of operation has shown very little improvement in deterioration of sorbents. The method offers no economic advantage, as the relatively large quantities of suspending mediums require a much larger quantity of heat during desorption.

After the cause of deterioration - loss of bonded water - had been discovered, several possible preventatives became apparent, the most promising being the use of moist inlet air during sorption; however, none of these methods has been investigated.

Presence of Water in Salcomine

In 1947 Diehl (30) reported the probable presence of water in salcomine and stated that its presence in the compound could not be proved or disproved by chemical analysis for lack of a satisfactory method of recrystallizing the compound for purification; nor by molecular weight determination, since 9 mass units (one-half mole H_2O per atom of Co) in 325 (molecular weight of salcomine) would result in questionable accuracy with compounds of variable purity. Removal of water at elevated temperatures for its determination by weight difference was equally difficult because of the decomposition of salcomine with liberation of salicylaldehyde. Determination of the chemical structure is complicated further by the presence of crystalline modifications of salcomine (27, 76) that have similar chemical compositions yet are completely inactive toward oxygen.

However, Diehl was able to show the presence of water by heating salcomine in anhydrous pyridine, collecting the distillate, and determining - by means of Karl Fisher reagent - the water expelled from the compound and distilled over with the pyridine. We have confirmed these results by a similar procedure. Using salcomine prepared by the Rumford Chemical Works and having an oxygen-carrying capacity of 4.32-percent we found 2.19, 2.16, and 2.20 percent water by weight; freshly prepared salcomine having an oxygen-carrying capacity of 4.8-percent showed, in corresponding successive tests, a water content of 2.31, 2.30, and 2.30 percent.

We developed a rapid direct method for determining the presence of water in salcomine. This qualitative test is based on the fact that pyridine replaces bonded water in the molecule. To a 2-gram sample of salcomine, which had been activated at 180° C. in vacuum for 2 hours, was added 30 ml. of anhydrous pyridine, prepared by distillation from potassium hydroxide pellets. The solution was heated, and the distillate (still protected from atmospheric moisture) was tested for water by red litmus paper. Pyridine changes the color of this indicator to blue in the presence of water only. Before addition to salcomine, pyridine had no effect on red litmus. The accuracy of this test was verified by repeated tests with intermediate blank runs.

Loss of Water During Deterioration

On repeated cycling at atmospheric pressure, a continuous decrease was observed in the amount of oxygen produced, which is typical of the results reported in the literature, as seen from table 7.

TABLE 7. - Deterioration of salcomine on cycling

Cycle No.	Sorption		Desorption at atmospheric pressure		
	Temp., ° C.	Pressure, atm. abs.	Temp., ° C.	Oxygen collected, ml.	Oxygen produced, weight-percent
1.....	26	1	152	172	4.41
12.....	27	1	150	160	4.08
25.....	29	1.1	175	162	4.13
44.....	29	1	158	155	3.96

Several subsequent experiments were so designed that the cause of this decreasing activity, presumably deterioration by loss of chemically combined water, might be verified. An apparatus was assembled, shown in figure 6, to pass pure, dried oxygen through salcomine at 100° C. with simultaneous measurement of changes in the sorptive capacity. Water removed from salcomine was collected in U-tubes filled with selective drying agents. Their gain in weight served as an indication of the amount of water lost. The data obtained from the train are as follows:

	Grams
Weight of salcomine sample after 844 hours:	14.4729
Weight of salcomine sample before test:....	13.8932
Gain in weight......................	.5797

Initial sorption capacity: 3.64% oxygen by weight.
Final capacity: 0%
Volume of oxygen used: 66 std. cu. ft. in 844 hours.
Rate of oxygen flow: 0.0013 std. c.f.m. = 0.61 ml./sec.

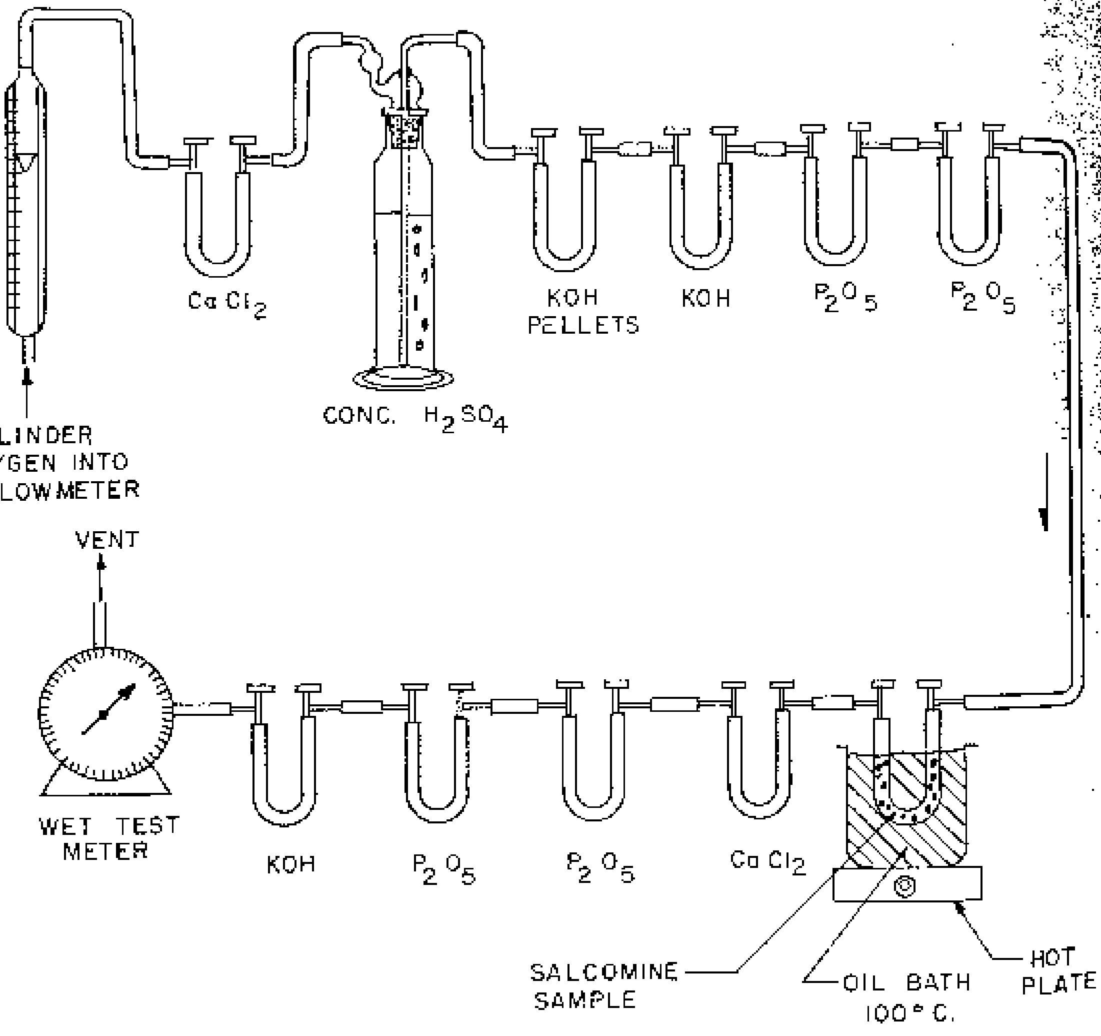


FIGURE 6. - Apparatus for Study of Deterioration of Salcomine at 100° C.

Figure 7 shows the decrease in sorption capacity and increase in weight of 13.8923 grams of salcomine with time of exposure to oxygen at 100° C. The sorbent gained 0.5797 gram (4.17 percent), indicating that oxygen was being picked up; that is, salcomine was undergoing destructive oxidation. The sample reached a constant weight after 844 hours. At that time the sorptive capacity, determined volumetrically, dropped to nil. The gain in weight of the U-tubes

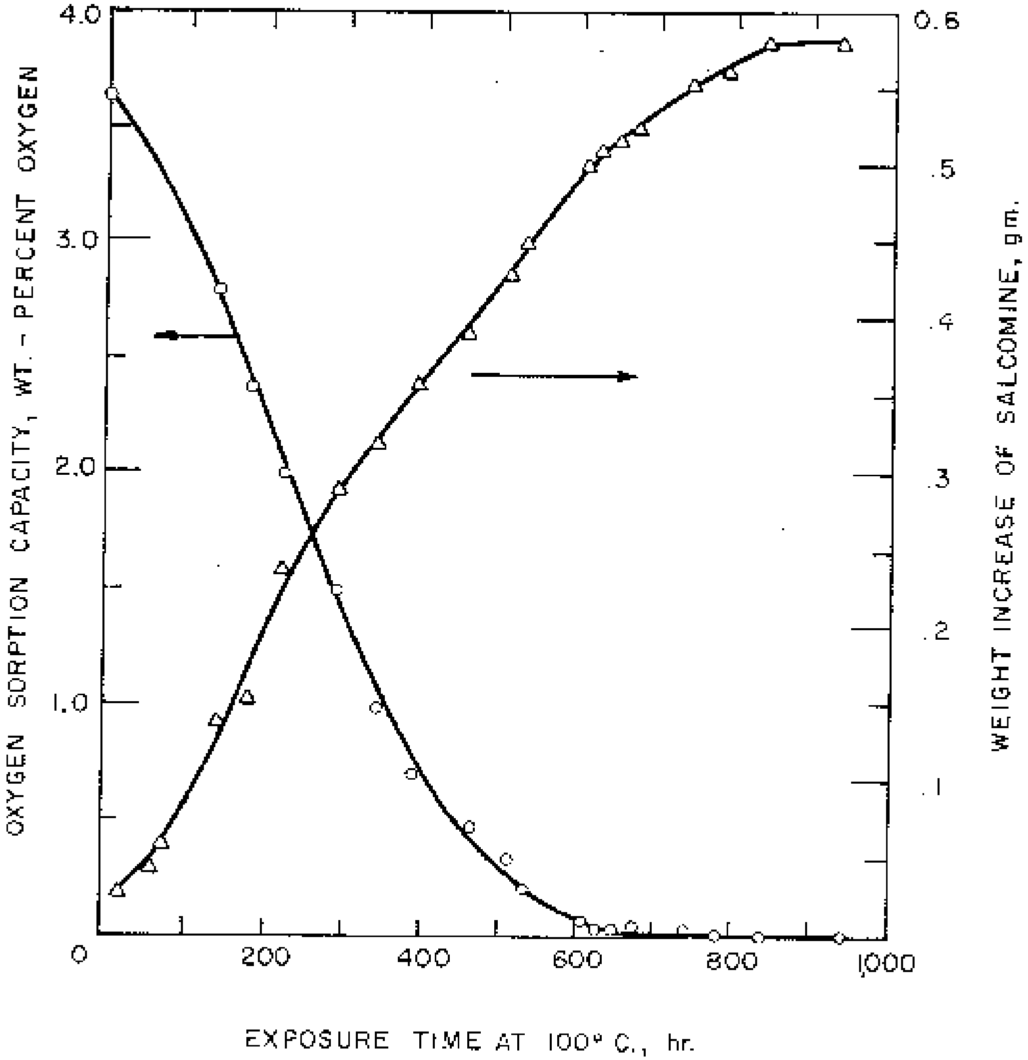


FIGURE 7. - Effect of Exposure Time to Oxygen on Sorption Capacity and Destructive Oxidation of Salcomine. (Original mass about 14 grams.)

in the train (fig. 6) may be attributed to water loss, and to a deposit of unknown material. The latter may have consisted of decomposition products resulting from the oxidation of the sorbent, thus invalidating this method for direct determination of water given up by salcomine. The drying agents at the time of complete deterioration had gained weight as follows:

	Grams
$CaCl_2$.....	0.6162
P_2O_5......	.6625
KOH.......	.5457
Total	1.8244

None of the desiccants reached a constant weight when the sorptive capacity of salcomine dropped to zero. This suggests that salcomine may have continued its slow, destructive oxidation with simultaneous loss of water, despite complete loss of activity for oxygen sorption (oxygenation). An appreciable amount of black decomposition products deposited at the inlet end of the P_2O_5 tube and a pink coloration were also noted. Presumably a decomposition product, possibly a basic gas, reacted with P_2O_5, while it left the preceding $CaCl_2$ unaffected. The KOH may have absorbed acidic gases resulting from the decomposition. The second P_2O_5-filled U-tube, serving as a check for the efficiency of removal by the first P_2O_5 tube remained constant in weight throughout the test run.

To relate the loss of water to deterioration, one must show that water is lost while deterioration is in progress, and that a completely deteriorated sample contains no coordinated water. A sample of salcomine, deteriorated completely over a period of several weeks until it would neither take up nor desorb oxygen, was found to be water-free by the pyridine-water replacement test. The sample could not be reactivated to any extent by adding water.

To show that loss of water occurs during "oxygenation" in cycling and not on exposure to elevated temperatures, we heated a fresh sample at 110° C. under a vacuum of less than 1 mm. of mercury for 55 hours. This sample suffered neither loss in weight, nor loss in activity. The cause of deterioration is thus reasonably well established as loss of a coordinated water-molecule, followed by the decomposition ("oxidation") of salcomine by pure oxygen.

DISCUSSION OF RESULTS

Salcomine was found to be the most promising oxygen carrier investigated. None of the versene-type compounds and other chelates investigated or any of the inorganic compounds previously proposed offer as favorable economic possibilities as salcomine.

Among the salcomine-type compounds investigated, the parent compound, bis-salicylaldehyde ethylenediimine cobalt, is the least expensive and has relatively favorable properties, except for its slow but still appreciable deterioration. Certain derivatives of this compound and those of type II (see fig. 1) perform better in cycling and deteriorates less, but are much more expensive. Of several hundred salcomine derivatives prepared by Calvin, Diehl, Geissman, and others (1, 9, 11, 23, 24, 41, 46), none appears to have economic advantages over the parent compound.

Structure and Deterioration of Salcomine

The deterioration of salcomine is intimately related to its chemical structure. The structure shown in figure 8 of an active oxygenated molecule of salcomine, postulated and discussed by Diehl (30), differs from earlier structures in that bridging groups or coordinating compounds connect two adjacent salcomine molecules. The structure might be doubted on grounds that no other case is known of a water molecule sharing more than one pair of electrons in coordination compounds.

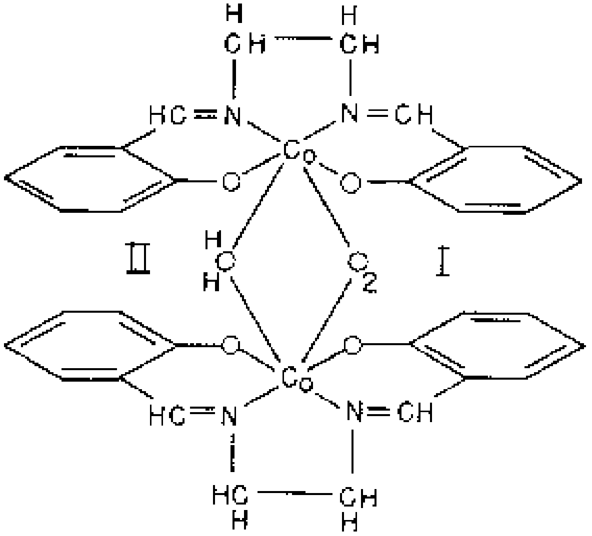


FIGURE 8. - Hypothetical Structural Formula of Salcomine.

During preparation of salcomine the coordinating group in position I is believed to be a solvent molecule (for example, pyridine or ethanol), which is removed during activation at 180° C. and 1 mm. pressure for 2 hours, leaving unbonded the sixth coordination bond of salcomine. This site is thought to be responsible for the reversible sorption of oxygen, forming the oxygenated compound shown in figure 8. The following list of reasons, based chiefly on Diehl's investigations and our own work, supports this theory:

1. When salcomine is synthesized in nonaqueous solvents, a complex coordination compound forms, similar to the structure in figure 8 but probably containing solvent molecules in both positions I and II. The stability of these compounds depends upon the polarity of the solvent molecules; with pyridine a fairly stable compound is formed, in alcohol a less stable one results, and that formed in benzene or xylene is very unstable. These compounds were completely inactive to oxygen sorption. Following activation, in which the solvent molecule in position I is removed, the compounds tend to be oxidized destructively, forming decomposition products, and will not reversibly react with oxygen. However, when the same compounds are prepared in nonaqueous solvents and subsequently treated with water, position I will be occupied by a solvent molecule and position II by a water molecule. On activation, this water-bearing compound loses the remaining solvent molecule and becomes a reversible sorbent for oxygen. Two examples of this behavior have been reported by Harrison and Diehl (57).

2. When salcomine is synthesized from a partly aqueous solvent (as 70-percent alcohol or 50-percent pyridine), the compound formed is similar or identical with salcomine prepared in nonaqueous solvent and subsequently treated with water; that is, a water molecule is bonded between the two cobalt atoms in position II, and position I is occupied by either an alcohol or pyridine molecule. This solvent molecule in position I appears to be quantitatively removed during activation, as measured by a suitable solvent absorber. An exact quantitative determination has not been possible because of impurities in the compound, and recrystallizations have led to further decomposition.

3. Pyridine can react with the active compound by displacing the water molecule in position II; the displaced water can be collected and measured. The pyridine-substituted compound no longer absorbs oxygen reversibly but is destructively oxidized like the compounds mentioned under point 1.

4. The deoxygenated form of active salcomine is paramagnetic; the oxygenated one is diamagnetic (15). Quantitative measurements indicate one unpaired electron per cobalt atom as expected from the proposed structure (with coordination position I not filled in the active deoxygenated form). To the 25 electrons around the bivalent cobalt atom are added 8 electrons from the 4 covalent linkages with the organic substance and 2 from the oxygen of the bridging water molecule, making a total of 35, the odd 4p electron remaining unpaired. The oxygen molecule is paramagnetic, having two unpaired electrons. Coupling of one oxygen molecule to two deoxygenated salcomine molecules probably involves pairing of the uncoupled electrons, two cobalt atoms being required for the two unpaired electrons of the oxygen molecule to form a diamagnetic compound.

5. An easily removed peroxo-linkage between two cobalt atoms forming a polynuclear coordination compound is well known. A process based on the recovery of oxygen from the atmosphere by acidification by bivalent cobalt salts in the presence of ammonia has been investigated by Clund, Keller, and Nordt (52), who concluded that the process was uneconomical because of the irreversible oxidation of bivalent cobalt to the trivalent state. A similar process using hexammine cobalt (II) chloride was patented by Warne and Woolcock (98). Their procedure was based on the expulsion of ammonia by oxygen, which was subsequently expelled from the peroxo-cobalt compound by increasing the ammonia concentration.

6. Because of the extreme difficulty of obtaining a pure salcomine compound, chemical analysis has not permitted an undisputable conclusion on the exact composition of salcomine. Confirmation of the binuclear composition of salcomine could be obtained from the molecular weight of the material. However, in addition to the difficulty with purification, replacement of the bonded-water molecule by solvent complicates molecular weight determinations by either the cryoscopic or the boiling-point method. Diehl and others (30), for example, found a depression of the boiling point instead of the expected elevation in chloroform and pyridine solvents. The apparent explanation was that water had been expelled from the compound. In any solvent that does not replace the water molecule, salcomine is too insoluble to give a significant change either in freezing or in boiling point. In the few solvents in which salcomine is slightly soluble, water is replaced by solvent.

One might determine the molecular weight of the solvent-substituted molecule after complete removal of water, or that of the inactive form of salcomine prepared anhydrously. A search of the literature indicates that no attempt has yet been made to determine the molecular weight of the inactive, solvent-substituted compound.

7. Loss of chemically combined water with subsequent oxidation has been shown to cause the slow deterioration during cycling. The sorptive capacity

of salcomine decreases in proportion to the loss of water. However, owing to a nearly simultaneous destructive oxidation, the additional water produced precludes exact correlation between water loss and decrease in sorptive capacity.

PROCESS ECONOMICS

To be competitive with conventional rectification of liquefied air, a process using an oxygen carrier must comply with all of the following conditions:

(1) For a sorbent or carrier compound having a molecular weight of 300 and a specific heat of 0.2 B.t.u./lb.-° F. (average values of several possible compounds), the difference between the temperatures of sorption and desorption should not exceed 400° to 500° F. A greater difference is economically prohibitive. For example, the cost of heating a permanganate mixture (containing 63 percent NaOH to keep the molten mass fluid), to produce 1 ton of oxygen is roughly $0.75 per 100° F. temperature difference.

(2) The heat of reaction should be reasonably low, the upper limit being about 300 B.t.u. per pound of sorbent, producing 0.04 pound of oxygen. This is equivalent to a reaction heat of 15 million B.t.u. per ton of oxygen produced, which must be removed during sorption and supplied during desorption. At $0.25 per million B.t.u. the total cost of supplying reaction heat would be $3.75 per ton of oxygen. Very little, if any, of this reaction heat is recoverable during sorption at the lower temperature.

(3) Oxygen must be absorbed from air at pressures below 60 p.s.i.g., because the cost of compressing 5 tons of air to this pressure is approximately $4.40, based on 0.01 per kw.-hr. (65).

(4) Oxygen should be desorbed at pressures above approximately 1 inch of mercury abs., as evacuation costs below this pressure become prohibitive.

(5) The process should be carried out in relatively simple equipment. For example, several processes proposed in the past require extensive systems for solvent recovery. Others require glass equipment that cannot be replaced by high-grade alloy steels because of corrosion. Solid sorbents must be easily handled granular or powdered form. Liquid sorbents must have a low vapor pressure. Obviously, the use of standard equipment or machinery is preferable whenever possible.

(6) The sorbent must not deteriorate appreciably on cycling. Based on 2,000 cycles required to produce 80 tons of oxygen per ton of salcomine, with the latter assumed to cost $5.00 per pound, deterioration, at a rate of only 0.001 percent per cycle, represents a cost of $2.50 per ton of oxygen.

Among inorganic oxygen carriers, the hot sodium manganate process merits consideration. The overall reaction taking place during oxygen sorption at 600° F. and desorption at 1,200°-1,400° F. is:

$$MnO_3 \rightleftarrows MnO_2 + 1/2\ O_2$$

However, the process is much more complicated. NaOH is added to keep the molten mass fluid, and an intricate heat-recovery system must be used. This results in excessive processing cost, as well as a high cost of investment. The process would thus exceed the economic limitations for several conditions listed above.

In comparison, the barium peroxide process frequently proposed and occasionally used in the past:

$$BaO + 1/2\ O_2 \rightleftarrows BaO_2$$

is within the economic limits of each condition enumerated above, except the first one. The cost of heating the sorbent material from 400° F., maintained during the sorption step, to 1,600° F. for desorption is prohibitive.

Alkali salts of pyrogallic acid are highly effective oxygen sorbents under any pressure at ordinary temperatures, but a high vacuum is required to release absorbed oxygen. Because of the lack of conformity with condition 4, such a process would also be prohibitive economically.

In comparison with the inorganic oxygen carriers discussed above, metal chelates comply much better with the conditions that define process economy.

Salcomine is well within the limitations of the first five conditions. However, for the time being its slight rate of deterioration places it beyond the economic limits, regardless of other cost factors.

Practical Process Principles

A preliminary cost estimate for a 200-ton-per-day oxygen plant using salcomine has shown that oxygen would cost at least $6 per ton, even with the most optimistic assumptions. Nevertheless, the salcomine process has a number of practical advantages:

1. Plants of any size or capacity can be constructed to produce commercial-grade oxygen. The equipment may be started to operate on short notice.

2. Once started, the unit produces oxygen almost immediately and is, thus, ideally adapted to intermittent service.

3. The plant can be provided with automatic process controls, including starting and stopping devices for all plant units in predetermined sequence. As a result, manpower requirements can be reduced to a minimum.

4. The equipment is light and compact, compared with conventional systems.

In view of these advantages, such a process might find application for producing oxygen on ships or planes, in isolated or temporary installations where oxygen is needed for cutting and welding or medical uses, and in special applications where cylinder oxygen cannot be readily supplied.

To avoid operating difficulties, such as clogging and local overheating, fluidization of salcomine appears to be one possibility. One advantage of fluidization is improved temperature control, which would tend to prevent local overheating and deterioration. Partial fluidization of the sorbent bed may be sufficient.

To make the process continuous, pairs of sorption towers can be connected to operate intermittently on complementary half cycles. While the sorbent vessel "on stream" selectively removed oxygen from the air, the "off-stream" vessel delivers it to a simple product-treating train and relief holders. Enough moist air would be passed through the on-stream vessel to keep the temperature below 30° C. until the salcomine became saturated with oxygen. Simultaneously, oxygen recycled from the storage holder may be preheated to 110°-115° C. and pulled by an exhauster-blower through the oxygen-saturated salcomine in the off-stream tower to heat this bed to 80°-85° C. at slightly below atmospheric pressure. Oxygen is desorbed from the bed under such conditions, that is, while the heat of sorption (20 kcal. per gram-mole O_2) is being transferred to the sorbent.

One disadvantage is that spent salcomine must be replaced at intervals. Also, fluidizing requires approximately 11 times as much air (to keep the bed below 30° C.) during sorption as would be necessary to simply saturate the salcomine. However, by this method of adding and removing heat from the sorbent, deterioration can be reduced considerably. Such a process would produce oxygen at $20-$30 per ton.

SAFETY CONSIDERATIONS

Granular salcomine contains a small amount of fines. The dust formed in handling should not be inhaled, as it irritates the respiratory system and gives symptons similar to those of a heavy head cold (72). In one case, such an irritation may have contributed to the death of a worker. In 1 year of experimental work at the Bureau of Mines, no difficulties were found in handling small quantities of salcomine (a few pounds) by normal laboratory procedures. Additional references to the toxicity of salcomine are listed in the bibliography (2, 19, 21, 41, 82, 96).

The handling of cylinder oxygen requires certain well-known safety precautions. In addition, the use of oxygen above room temperature requires additional precautions because of the higher reactivity of heated oxygen. In our experimental work, involving only relatively small quantities of materials, no precautions were necessary beyond normal safety practices.

In pilot-plant work with salcomine (44), at temperatures up to 110° C., the only corrosion reported was of copper tubes in the cooling system at the silver-soldered return-bend joints. They were replaced by cupronickel tubes after about 3 months of operation.

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37. DIEHL, H., HACH, C. C., HARRISON, G. C., LIGGETT, L. M., AND BROUNS, R. J. Studies on Oxygen-Carrying Cobalt Compounds. XIII. Apparatus for Determining the Capacity and Rate of Oxygenation of Solid Materials. Iowa State College Jour. Sci., vol. 22, Mar. 4, 1947, pp. 150-164.

Presents diagrams of three volumetric apparatus used for measuring the rate of oxygenation of cobalt chelates. Also includes a diagram of a manometric apparatus for determining capacity. Gives seven methods for determining the capacity and rate of oxygenation, including three methods for capacity determination: Direct gravimetric method, gas-evolution nitrometer method, and differential manometric apparatus.

38. DIEHL, H., AND HENN, J. The Presence of Water in Oxygen-Carrying Cobalt Compounds. Iowa State College Jour. Sci., vol. 23, 1949, pp. 273-278.

Describes a method for determining chemically bound water by titrating with "Karl Fischer reagent." Two different tests indicated approximately 1/2 mol of water per each atom of cobalt.

39. DU PONT DE NEMOURS & CO., E. I. Final Report on Analysis and Degradation Study of Salcomine. OSRD 1951, PB 9395, Oct. 25, 1943.

Reports methods for the quantitative analysis of fresh as well as degraded salcomine; the results of these analyses are given. Proposes a mechanism for the formation of the observed degradation fragments.

40. FEBER, R. C., JR. A Polarographic Study of Some Metal Inner Complex Salts. Ph.D. thesis, University of California, Berkeley, 1947.

Presents the results of a study on polarographic reduction potentials of oxygen in the presence of various salicylaldehyde alkylene diamine derivatives.

41. FIELD, E., BELL, C. D., AND HARDY, J. V. E. Salcomine as an Absorbent for Separating Atmospheric Oxygen. OSRD 1616, PB 9388, July 16, 1943, pp. 44-45.

Reports investigations by the du Pont Co. Describes a pilot plant for producing oxygen with a circulating suspension of salcomine in oil. Studies were made also of chemical structure, reaction rates, and life of sorbent. The system had no advantages in weight and bulk over dry-bed operation. Especially noteworthy is a brief discussion of safety hazards with salcomine.

42. FIELD, E., AND SMITH, D. M. Investigations for Oct. 1-Dec. 12, 1942. OEMsr-604.

43. FOGLER, B. B., AND MAREK, L. F. Process for Production of Oxygen. U. S. Patent 2,450,276, Sept. 28, 1948.

Describes oxygen absorption-desorption by a chemical oxygen carrier. Discusses salcomine and its derivatives in detail.

44. FOGLER, B. B. Regenerative Unit for Generating Oxygen. Ind. Eng. Chem., vol. 39, 1947, pp. 1353-1360.

A report on the study of salcomine for producing oxygen of sufficient purity for cutting and welding. The study includes selection of heat transfer equipment for cooling and heating sorbent and preferred operating cycles to obtain high hourly yields and long operating life for the sorbent. Discusses design and operating characteristics of a pilot unit having an average production capacity of 260 cubic feet of oxygen of 98-99% purity. 23 references.

45. FURNESS, W., CRAWSHAW, R., AND DAVIES, W. C. Polarographic Determination of Ethylenediamine-Tetraacetic Acid. Analyst, vol. 74, 1949, pp. 629-635.

46. GEISSMAN, T. A. Oxygen-Carrying Metallic Complexes of the Salcomine Type. OSRD 5927, PB 8613, OEMsr-934, June 30, 1945, 139 pp.

Covers the chemistry of salcomine and related compounds, including the effect of chemical structure upon activity; the manufacture of salcomine and related compounds, and oxygenation-deoxygenation reactions are discussed. Other subjects include a process-engineering evaluation, a discussion of the thermal properties of salcomine, methods of operation by cycling, and deterioration of salcomine. Final report under contract with University of California.

47. GEISSMAN, T. A., AND OTHERS. Preparation of Intermediates for Oxygen-Carrying Chelate Complexes. OSRD 4845, PB 9378, Mar. 23, 1945.

In this report the authors review and summarize their findings. A number of compounds, embracing a variety of structural types, have been prepared as possible substitutes for salicylaldehyde in salcomine. An attempt was made to establish the structural requirements for activity in complexes of the salcomine type and thus to furnish a logical basis for the design of highly active oxygen-carriers. A preliminary study was made of the potentialities of transannular perioxide of substituted anthracenes as practical oxygen-producing substances. No final conclusions were reached, except that these compounds showed some promise and further study might demonstrate methods by which they could be used. Deterioration in use of salcomine and ethomine was studied from the standpoint of chemical changes involved in degradation. A number of factors were recognized, the control of which in selecting the operating conditions is of great importance in the efficient utilization of these complexes.

48. GEISSMAN, T. A., SCHLATTER, M. J., WEBB, I. D., AND ROBERTS, J. D. The Synthesis of Some Intermediates for Use in the Preparation of Analogues of Salicylaldehyde Ethylenediimine Cobalt (Salcomine). Jour. Org. Chem., vol. 11, 1946, pp. 741-750.

Describes preparations of a number of aromatic and heterocyclic *o*-hydroxyaldehydes and some 2-(*o*-hydroxyphenyl) pyridine derivatives. All were of the salcomine type; emphasis was placed on development of metal chelates of greater stability than that of salcomine.

49. GILLILAND, E. R. Investigation of Oxygen Supply. Progress Report to Nov. 1, 1941. OSRD 291, PB 8311, Dec. 8, 1941.

Experiments were chiefly concerned with a study of the cobalt acetate-salicylaldehyde-ethylenediimine chelate reported by Tsumaki and Calvin. Reports the principal features of the design of a self-contained cycling unit to produce 4 cubic feet of oxygen per minute.

50. GILLILAND, E. R., AND OTHERS. Investigation of Oxygen Supply. OSRD 439, PB 8312, Mar. 1, 1942.

Reports further progress on the development of chemical sorption units for producing oxygen, including detailed design calculations for packed-tube and finned-tube units, and construction for the Naval Research Laboratory of a unit producing 5 cu. ft. of oxygen per minute. Charts and schematic diagram.

51. _____. Investigation of Oxygen Supply. OSRD 613, PB 8313, May 31, 1942.

Describes the separation of atmospheric oxygen with salcomine under various conditions of operation, and a test unit. Tables and graphs.

52. GLUUD, W., KELLER, K., AND NORDT, H. (The Production of Oxygen by Means of Ammoniacal Cobalt Solutions.) Ber. Gesell. Kohlentechnol., vol. 4, 1933, pp. 210-254.

53. HACH, C. C., AND DIEHL, H. Studies on Oxygen-Carrying Cobalt Compounds. XIV. The Design of Apparatus for the Manufacture of Oxygen Using Co-Ox and Its Derivatives. Iowa State College Jour. Sci., vol. 22, 1948, pp. 165-176.

Reports the design of an apparatus for manufacturing oxygen, using Co-Ox or its derivatives. Diagrams and describes the temperature-variation process and the adiabatic process in detail.

54. HACH, C., AND DIEHL, H. A Circulating Solid Apparatus for Manufacture of Oxygen. OSRD 1913, PB 9394, May 20, 1943.

Describes development of a circulating-solid type of apparatus for the extraction of atmospheric oxygen by oxygenation of a highly hydroscopic compound at room temperature, followed by deoxygenation at a higher temperature, both processes taking place at atmospheric pressure. Blueprint drawings, diagrams, and photographs.

55. HACH, C. C., LIGGETT, L. M., AND DIEHL, H. V. Studies on Oxygen-Carrying Cobalt Compounds. Di-(2-hydroxy-3-nitrobenzal)-ethylenediimine Cobalt. 3-Nitro Co-Ox. Iowa State College Jour. Sci., vol. 21, 1947, pp. 316-325.

Reports preparation and properties of 3-Nitro Co-Ox in detail.

56. HARLE, O. L., AND CALVIN, M. The Oxygen-Carrying Synthetic Chelate Compounds. VI. Equilibrium in Solution. Jour. Am. Chem. Soc., vol. 68, 1946, p. 2612.

Equilibrium has been measured for reversible oxygenation of certain cobalt chelates dissolved in organic solvents. Describes the apparatus, including the reaction vessel, which is shown in diagram.

57. HARRISON, G. C., AND DIEHL, H. Oxygen Problem. XXIV, Report 20 to NDRC, Iowa State College. OEMsr-215, PB 98622, July 1942.

Reviews a study of the reaction of cobalt chloride and disalicylalethylenediimine under anhydrous conditions.

58. _____. Oxygen-Carrying Cobalt Compounds. IV. The Reaction of Disalicylalethylenediimine and Cobalt Chloride Under Anhydrous Conditions. Iowa State College Jour. Sci., vol. 21, 1947, pp. 311-315.

Reactions of disalicylalethylenediimine and cobalt chloride under anhydrous conditions led to an inactive compound which did not absorb oxygen at 200 lb. pressure. However, it was converted to Co-Ox [bis(N,N'-disalicylalethylenediimine)-μ-aquo-dicobalt] by treatment with water.

59. HEAD, J., HACH, C., AND DIEHL, H. Oxygen Problem Report XXI. Iowa State College, OEMsr-215, PB 98733, May 1942.

Among the various compounds investigated, propylenediamine, phenylenediamine, decamethylenediamine, hexamethylenediamine, nonamethylenediamine, and benzidine proved to be satisfactory intermediates in the chelation of cobalt and other metals.

60. HENSELMEIER, L., AND DIEHL, H. Oxygen Problem XVII. Iowa State College, Rept. 13 to NDRC, OEMsr-215, PB 98734, April 1942, 20 pp.

Describes preparation of substituted ethylenediamine-cobalt compounds.

61. HETHERINGTON, C. L., AND CATTERALL, W. E. Special Engineering System Utilizing Chelate Chemical Absorbents for Oxygen Production. OSRD 1579, PB 9402, July 9, 1943, 152 pp.

Deals with technical and engineering phases of oxygen-generating equipment. The main problem was heat transfer. Several recommendations are made as to construction of oxygen-producing units to meet both theoretical and practical requirements.

62. HOLST, K. A. Preparation and Properties of Mixed Aldehyde Cobalt Derivatives. Rumford Chem. Co., East Providence, R. I., OEMsr-605, PB 98689, January 1943, p. 21.

Manufacturing procedures have been developed for the production of salcomine, methomine, and ethomine to be used for separating atmospheric oxygen. These, together with testing methods and other chemical studies, are reported in detail.

63. _____. Production of Salcomine and Related Compounds. OSRD 6052, PB 8601, Oct. 1, 1945.

Reports in detail manufacturing procedures for salcomine, methomine, and ethomine; also describes test methods and related chemical studies. Gives a procedure for preparing 50-pound batches of salcomine and preparing methomine and ethomine.

64. HUGHES, E. W., WILMARTH, W. K., AND CALVIN, M. The Oxygen-Carrying Synthetic Chelate Compounds. V. Equilibrium With the Solid Compounds. Jour. Am. Chem. Soc., vol. 68, 1946, p. 2273.

Equilibrium pressures of oxygen over four crystalline oxygen-carrying chelates have been measured as a function of degree of oxygenation. X-ray powder diagrams were made for one of these compounds after oxygen sorption, with extent of oxygenation ranging from 0 to 92 percent.

65. KATELL, S., AND MCGEE, J. P. An Economic Study of Air-Compression Costs. Cost Engineering, vol. 2, No. 1, 1957, pp. 5-9.

Estimates costs of air compression up to 120 p.s.i.g. for various-size units. Tables and graphs.

66. LATIMER, W. M. The Production of Oxygen by Use of a Regenerative Chemical. OSRD 64, PB 8314, 1941.

Describes the properties of salcomine, although much detail included in the more complete final reports has been omitted.

67. LIGGETT, L. M. AND DIEHL, H. The Duff Reaction for the Preparation of Hydroxy Aldehydes. Proc. Iowa Acad. Sci., vol. 52, 1945, pp. 191-197.

68. _____. Studies on Oxygen-Carrying Cobalt Compounds. XII. An Attempted Synthesis of an Unsymmetric Schiff's Base of Ethylenediamine. Iowa State College Jour. Sci., vol. 22, 1948, pp. 141-149.

Differences between mixed condensation products of aldehydes, ethylenediamine, with cobalt compounds and any pure compound aroused curiosity regarding the possible behavior of a cobalt compound formed by condensing two different aldehydes to form an unsymmetric molecule. No stable unsymmetric Schiff base could be prepared.

69. _____. Oxygen Problem. XLV. Iowa State College, OEMsr-215, PB 98697, September 1942.

Presents the results of various experiments pertaining to oxygen production. Di(salicylal) methylenediimine and its cobalt derivatives were prepared. Two samples of Co-Ox were analyzed for oxygen and moisture content.

70. LIGGETT, L. M. AND OTHERS. Oxygen Problem. XXXVIII. PB 98621, July 1942.

The known methods of preparing di(2-hydroxy-3-methoxybenzal) ethylenediimine cobalt (CO-Ox M) were studied and certain improvements made. Apparatus was assembled for producing 30 pounds per day, and the recommended procedure was tested. Both the deoxygenated and the oxygenated forms of Co-Ox M were very hygroscopic.

71. LITTLE, A. D., INC. Final Report on Development of Test Unit for Production of Oxygen by Regenerative Chemical. Cambridge, Mass., Jan. 31, 1944.

72. _____. Report on the Effect of Salcomine on Workmen With Summaries of Physical Examination. OEMsr-269, Feb. 1, 1944.

73. LOBO, W. E., AND BOCKIUS, C. Oxygen Plant Development Employing Regenerative Chemicals. OSRD 5154, PB 8339, May 31, 1945.

Authors describe a plant for separating oxygen from air by means of salcomine, and related research. The report contains a bibliography, pertinent correspondence, memoranda, reports, and specifications dealing with equipment details and operating experiments. Detailed process calculations and a list of all drawings are shown for the shipboard unit.

74. LONGWELL, J. P., AND CATTERALL, W. E. The Regenerative Chemical System for Oxygen Production on Board Aircraft. VII. OSRD 1620, July 19, 1943.

Describes development of an aircraft-carried oxygen-producing unit employing organic sorbents. This development was discontinued because of indication of unsatisfactory weight for chemical equipment compared with the weight of a Collins unit based on the mechanical production of oxygen. It was concluded that for aircraft, liquid-oxygen storage is superior to any other system.

75. LYONS, C. J., AND BATCHELDER, H. R. Tonnage Oxygen Production, 1956. Am. Gas Assoc. Operating Sec. Paper CEP-56-16, May 16-18, 1956.

76. MARTELL, E. Metal Chelate Compounds. Dept. of Chemistry, Clark University, Worcester, Mass. From Annual Review of Physical Chemistry, vol. 6, 1955, pp. 239-260.

Includes bibliography of 72 references.

77. MARTELL, A. E., AND CALVIN, M. Chemistry of the Metal Chelate Compounds. Prentice Hall, Inc., New York, N. Y., 1952, pp. 336-352.

Discusses the mechanism of oxygen sorption and desorption by several chelates in detail. Presents several physical measurement studies. Sections are devoted to crystal structure and polarographic studies.

78. MATHEWS, J., AND DIEHL, H. Oxygen Problem. XLIV. OEMsr-215, PB 98696, September 1942, 6 pp.

Hexa-allylamine peroxodihydrozoic cobalt-trichloride and its intermediate were prepared by the authors, but this sorbent did not sorb oxygen reversibly.

79. MATTHEW, C. J. Development of Test Unit for Production of Oxygen by a Regenerative Chemical. XI. OSRD 5150, PB 8343, May 31, 1945.

An account of difficulties in engineering a test unit for producing oxygen in the limited space on board warships. Recommendations are given for improvements in design.

80. PFEIFFER, P., BREITH, E., LUBBE, E., AND TSUMAKI, T. (Tricyclic Ortho-Condensed Partial Valence Rings.) Ann. Chemie (Liebig), vol. 503, 1933, pp. 84-130.

Discusses three types of partial valence rings, generally recognized, and gives examples of Ni, Cu, and Fe compounds prepared in their studies.

81. PFEIFFER, P., AND GLASER, H. (Exchange of the Amine Residue in the Inner Complex Salts of Schiff Bases.) J. prakt. Chem., vol. 153, 1939, pp. 265-284.

This report describes preparation of the salcomine molecule with an atom of Cu instead of Co in the molecule.

82. RENSHAW, B. Summary Report on Miscellaneous Toxicological Studies. OSRD 5669, PB 5927, Sept. 13, 1945.

This report describes studies on the toxicity of salcomine dusts, which were one-fourth to one-twentieth as toxic as mustard-gas vapor. With reasonable precautions, including use of dust respirators, no marked industrial hazard can be expected.

83. RUSHTON, J. H., AND OTHERS. Central Eng. Lab., Nat. Defense Research Committee (Oxygen). OSRD 4452, PB 19659, Oct. 1 to 31, 1944.

The authors describe, in six reports, research for submarines pertaining to four main categories: mechanical units for oxygen production; chemical units for oxygen production; submarine air conditioning; miscellaneous problems. Salcomine units are included.

84. RUSHTON, J. H., AND OTHERS. Central Eng. Lab., Nat. Defense Research Committee (Oxygen). Mar. 1, 1944 through March 1945, except October 1944. OSRD 4732, 4879, 5040, 4516, 4623, 4207, 4142, 3523, 3652, 3760, 3861, 3972, 4302; PB 9377, 1944-45.

These 13 progress reports for March 1944 to March 1945 describe work undertaken at the University of Pennsylvania on the problem of oxygen production by chemical and other means. The work covered: (1) Low-pressure units - oxygen pilot plant; airborne oxygen unit, liquid-oxygen plant for submarine propulsion, etc. (2) High-pressure oxygen unit for liquefied gas (LeRouget cycle). (3) Chemical units, single-case salcomine pilot-plant, peroxide oxygen-generator and chlorate candles, regenerative salcomine chemicals, and liquid oxygen vaporizers. (4) Submarine air conditioning; removal of CO_2 from air. (5) Miscellaneous removal of acetylene and other hydrocarbons from compressed air; liquid oxygen vaporizers, rectifying column problems, equilibrium systems for oxygen-nitrogen and oxygen-argon.

85. SCHWANDT, R. W. AND DIEHL, H. Oxygen Problem. XXXV. Iowa State College. OEMsr-215, PB 98703, August 1942.

The identity and purity of tetramethylenediamine were determined. Tetramethylenediamine and salicylaldehyde were condensed. The product, disalicylaltetra-methylene-ethylene-diimine, was characterized. The oxygen-carrying properties of disalicylalethylenediimine-cobalt were destroyed when other diamines were substituted for ethylenediamine.

86. SMETS, G. (Chelate Compounds.) Chem. Zentralb. II (1943), vol. 708, pp. 97-107.

A review of the literature, with emphasis on polarographic studies.

87. SMITH, A. M. Deterioration of the Organic Oxygen Absorbents Salcomine and Ethomine. Massachusetts Inst. Technol. Rept., 1943.

Similar to later reports.

88. SMITH, A. M., AND CATTERALL, W. E. Properties of Salcomine and Ethomine and the Separation of Atmospheric Oxygen Therewith. OSRD 1539, PB 8347, June 25, 1943.

A detailed coverage of studies made from an engineering standpoint of the properties of salcomine and ethomine and their use in a cyclic system for absorbing atmospheric oxygen. A study is included of the various factors influencing capacity and reactivity of these compounds. Sample calculations are presented. The introduction and procedure sections present information concerning apparatus. Sorption rate curves are presented.

89. SQUIRES, L. Summary of Investigations for September 1942. OEMsr-604.

90. TSUCHIDA, R., AND TSUMAKI, T. (Absorption Spectra of Salicylaldehyde-ethylenediimine and Related Compounds.) Bull. Chem. Soc. Japan, vol. 13, 1938, pp. 252, 527-533.

Absorption spectra were measured; the spectra are qualitatively explained by the theories of absorption spectra of coordinated compounds.

91. TSUMAKI, TOKUICHI. (Some Iron Compounds With Secondary Valency Rings.) Jour. Chem. Soc. Japan, vol. 55, 1934, pp. 1245-1251. Bull Chem. Soc. Japan, vol. 10, 1935, pp. 74-81. (In German.)

92. ______. (Coordinate Valency Rings. III. Some Inner Complex Salts of Iron and Manganese.) Jour. Chem. Soc. Japan, vol. 56, 1935, pp. 1329-1331.

93. _____. (Coordinate Valency Rings. IV. Some Inner Complex Salts of Hydroxyaldimines.) Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 1288-1294. Bull. Chem. Soc. Japan, vol. 13, 1938, pp. 252-260.

Discusses certain derivatives of salcomine.

94. UENO, K., AND MARTELL, A. E. Infrared Study of Metal Chelates of Bis-acetylacetone-ethylenediimine and Related Compounds. Jour. Phys. Chem., vol. 59, October 1955, p. 998.

95. U. S. NATIONAL DEFENSE RESEARCH COMMITTEE. Oxygen Problems. Research on Oxygen Generation and Utilization for Military Purposes. Summery Tech. Rept. PB 30482.

Describes research on generation and use of oxygen for military purposes. The following aspects of the problem were investigated: (1) Development of compact, lightweight portable units for separating oxygen from air; (2) development of equipment for supplying oxygen for specialized uses, such as aircraft breathing, and development of instruments for testing oxygen intended for the specialized uses; (3) generation of oxygen aboard submarines for use as a secondary fuel, and operation of internal combustion engines while submerged.

A detailed study was made of liquid-air cycles and equipment for separating atmospheric oxygen. The possibility was studied of utilizing organic chelate compounds which had a reversible action with oxygen. Salcomine and substituted salcomine compounds, such as ethomine, methomine and fluomine, were considered. Tables of data on many of these compounds are shown. The process utilizing the chelates was inefficient compared with units based on rectification of liquefied air. Nevertheless, a unit was developed and tested for shipboard use for cutting and welding-oxygen supply. Several systems were studied for generating oxygen from chemicals.

96. U. S. NATIONAL DEFENSE RESEARCH COMMITTEE. Month. Prog. Reports on Toxicity of Chemical Warfare Agents. University of Chicago Toxicity Laboratory, E. M. K. Geiling. Inf. NDCrc-132, Oct. 10, 1944, pp. 21-25.

97. VON BERG, R. L., AND CATTERALL, W. E. Characteristics of the Oxygen Absorbents Ethomine and Fluomine. OSRD 5407, PB 8346, 1945.

Describes the behavior of air-or-oxygen-ethomine and air-or-oxygen-fluomine systems. The purpose of the research was (1) to obtain data for designing large-scale units utilizing ethomine and fluomine; (2) to collect data for predicting the behavior of a given system with respect to variables such as temperature, pressure, chemical composition, and time. A list of references is included.

98. WARNE, K. C. AND WOOLCOCK, J. W. Recovery of Oxygen From Gaseous Mixtures, U. S. Patent 2,217,850. Oct. 15, 1940.

99. WEINKAUFF, O. J., AND KYRIDES, L. P. Process for Producing *o*-Ethavan. OSRD 1580, PB 8602, OEMsr-903, 1943.

Ethavan is the trade name for commercial ethoxy-hydroxy-benzaldehyde, an intermediate required in the production of the oxygen-absorbent ethomine. The paper describes a workable process for the industrial manufacture of Ethavan, from Ethacol (3-ethoxy-4-hydroxy benzene), through its orthoallyl-ether.

100. WHEELER, T. L. AND FOGLER, B. Development of a Test Unit for Production of Oxygen by Regenerative Chemicals. OSRD 3359, PB 9406, OEMsr-269, Jan. 31, 1944.

Final report on work by Arthur D. Little, Inc., in developing an oxygen-producing unit. The report covers studies of engineering variables. Equipment is recommended to carry out such a process when employing certain chelates. Describes a shipboard unit in detail. This report also covers work on several related problems: Evaluation of apparatus for measuring rates of aborption of chelates, investigation of an oxygen purity tester based on the use of regenerative chelates, and a brief study of contaminants in the oxygen produced with regenerative chelates.

101. WILMARTH, W. K., ARANOFF, S., AND CALVIN, M. The Oxygen-Carrying Synthetic Chelate Compounds. III. Cycling Properties and Oxygen Production. Jour. Am. Chem. Soc., vol. 68, 1946, p. 2263.

Discusses factors that influence the cycling properties and stability of CoSaEn and 3-F-CoSaEn chelates; the causes of deterioration of CoSaEn are analyzed and deterioration graphs are shown; and presents some x-ray diffraction data on the fresh and deteriorated sorbent.