730082

CONFIDENTIAL

N.D.R.C., Division B, December, 1942

PHYSICAL-CHEMICAL AND CHEMICAL ENGINEERING PROBLEMS
Summary of Progress from October 15 to November 15, 1942

Subsection B-7-B: Oxygen Problems -- E. P. Stevenson, Chairman.

SALCOMINE

Problem NL-B42 Development of Chemicals and Apparatus for Regenerative Production of Oxygen.

Problem AC-12: Manufacture of Oxygen while in Flight for Use of the Combat Crew.

Problem NA-111: Portable Unit for Supplying Oxygen.

Problem NS-116: Portable Unit for Producing Oxygen for Welding and Cutting and for Breathing Oxygen aboard Aircraft.

Problem NS-117: Oxygen Producing Apparatus for Repair Ship Installation.

Problem CE-29: Field Generation of Oxygen Gas.

Progress Report: Serial No. 396, April 15 to September 1, "Development of Oxygen Carrying Chemical", by Harvey Diehl.

Serial No. 398, August 1 to September 1, "Chelate Oxygen Compounds and Mechanism of the Absorption Reaction", by Melvin Calvin.

CLASSIFICATION CANCELLED OR CHANGED TO Unclassified
BY AUTH. CE DAR.1 1.1
[illegible] DATE 3/6/96
[illegible] 3/1/96

Preparation and Equivalents

Preliminary studies of the effect of mixing two of the aldehydes which yielded successful oxygen carrying compounds and forming the cobalt derivative of the mixture were carried out using an equi-molecular mixture of salicylaldehyde and 2-hydroxy-[illegible] benzaldehyde, [illegible] this mixture with ethylene-[illegible] and forming the [illegible] of the Schiff's base so [illegible] material absorbed [illegible] spontaneously at room tempera-[illegible] below room temperature, [illegible] 3-methoxy compound. Tempera-[illegible] required to deoxygenate the pure [illegible] respectively. It appears, therefore [illegible] oxygen-pressure-temperature [illegible] temperature scale in a [illegible] points". Similarly, salicyl-[illegible] aldehyde when mixed and [illegible] hydroxy-3-methoxy benzal-[illegible] which differed markedly [illegible]

CONFIDENTIAL

A number of new intermediate materials as well as the cobalt chelate compounds therefrom have been synthesized, but so far the results have not been very impressive other than the mixed compounds reported above. A program is contemplated for the study of the effect of substituting a hererocyclic molecule containing also hydroxyl and aldehyde groups in the salicylaldehyde part of the Salcomine molecule; it is hoped that this will lead to a more stable chelate material.

The rate of oxygen uptake of a 3-ethoxy compound is being investigated in pure oxygen at pressures less than one atmosphere. Both the rate and equilibrium values of oxidation decrease with decreasing pressure. The rate at 13 centimeters of pure oxygen is substantially the same rate of oxidation for air at atmospheric pressure and 20°C. previously reported, although there appears to be some discrepancy in other reported rates of absorption. For example, in studies of oxidation with air, an increasing rate with temperature, with a maximum rate of approximately 50°C. has been reported by M.I.T., while Iowa State finds almost a constant rate from 0-20°C. Furthermore, Iowa State reports that it required almost two hours for complete peroxide formation with pure oxygen at one atmosphere absolute and 20°C., whereas the University of California found that samples are essentially completely oxidized in less than ten minutes under these conditions.

Cobalt-3-chloro-salicyl-propylenetriamine was found to desorb readily at room temperature with absorption requires from 140 to 165 P.S.I. oxygen partial pressure at 0°C.

An effort is being made to standardize the test procedure on Salcomine and related materials in order that a direct comparison may be had between results from various laboratories now engaged upon these studies.

It has been decided to drop further experimental work on the transannular peroxides as a method of separating oxygen from the atmosphere, in order that the research energy may be directed towards problems of more immediate interest.

[illegible] of the heats of oxygenation has [illegible] Salcomine of 22.5 kg. [illegible] The corresponding [illegible] in the range of [illegible] in the heat of the reaction with [illegible] to be one of the important [illegible] the suspected phase changes during [illegible]

[illegible] active crystals for both X-ray and [illegible] The micrographs show a decided [illegible] of active crystals after one cycle [illegible]

1263557

The x-ray studies are beginning to yield a good deal of information concerning mechanism of peroxide formation. It has been established that a phase change occurs in Salcomine if 4% or 5% of total oxygen is absorbed. This initially oxidized phase contains only about 3.9% oxygen (75% to 80% is theoretical) and it grows in volume at this per cent oxidation until the unoxidized phase has completely disappeared. The oxidized phase, containing 3.9% oxygen, is unable to absorb approximately 25% more oxygen without further phase change. Further knowledge of the arrangement of molecules in an active crystal is being sought through a study of x-ray pattern. The evidence continues to indicate the presence of a second active form in the parent compound.

Life Tests

Studies of the deterioration of Salcomine under a variety of absorption conditions using dried air, but under substantially the same desorption conditions, have shown reasonably good correlation, in that the deterioration is a function mainly of the amount of oxygen produced. Some exceptions, however, have been noted, among which is a somewhat greater deterioration at 250 lbs. air pressure with wet air, and at the higher temperature. Furthermore, there seems to be an acceleration of the deterioration after the compound has carried about ten times its weight of oxygen.

It would appear that the deterioration of the Salcomine is due partly to the chemical change involving deep-seated destruction of the Salcomine molecule and partly (chiefly) to a change which involves a change in either crystal structure or valence configuration without an actual loss of recoverable constituents of the Salcomine. The change from active to inactive form may also be due to a change in the molecule itself.

A rapid method of analysis of Salcomine is being developed which assists materially in the study of the deterioration of this material. Present indications are that the complete method may be able to differentiate between cobaltic and cobaltous cobalt in addition to determining the amounts of salicylaldehyde, ethylenediamine, [illegible] etc., which can be recovered.

[illegible] derivative has been shown to [illegible] pressure, lower- [illegible] the compound, [illegible] the [illegible] oxygen, and [illegible] deterioration [illegible] desorption [illegible] as the [illegible] to dry thoroughly [illegible] the opera- [illegible] beating in [illegible]

1263558

A 10% suspension of Salcomine in white oil vigorously shaken so as to be in constant contact with oxygen lost 15% of its activity in 15 hours, but remained almost constant in activity for another 30 hours. In another test in which absorption and desorption were allowed to take place on a 20% suspension, the activity of the sample fell off about 10% per 100 cycles and a considerable increase in viscosity was observed after 240 cycles, whether the absorption was allowed to take place at 15° or 30°C.

A suspension of Salcomine in silicon oil seems to be somewhat more stable than in white oil. There was apparently no decrease in the activity after heating for 41 hours at 100°C. in the presence of oxygen. However, after 89 hours the activity had dropped approximately 5%. Silicon oil suspensions seem to absorb little or no oxygen during the deterioration test (such absorption was observed in the case of the white oil suspension). An appreciable induction period (approximately 5 minutes) was observed in the absorption of oxygen in silicon oil suspension, whereas no such period of induction was observed in the white oil.

A Study of Oxygen Producing Cycles

The circulating solid apparatus for handling the methoxy derivative of Salcomine has now been completely redesigned and construction of the new model begun. The new model will be smaller and will be engineered for [illegible] operation and greater oxygen production. It is planned to make exhaustive studies of the operation of such apparatus over long periods of time once the construction is completed. The deterioration of the methoxy derivative subjected to continuous [illegible] cycling in an inert atmosphere is being [illegible]

It was [illegible] that perhaps the [illegible] of oxygenation would be [illegible] of the material consequently [illegible] with water and [illegible] with water. Some preliminary [illegible] show that [illegible] content of [illegible] of about 1.8% [illegible] at 100° and 40° [illegible]

[illegible] suspended [illegible]

1263559

The absorption and desorption properties of the ethoxy derivative of Salcomine have been evaluated and have been found very favorable for application to an aircraft unit. In the temperature region of 15°C. to 45°C. uniformly good absorption at the rate of 1.7 weight per cent oxygen absorbed from atmospheric air in five minutes is obtained. Its desorption is similar to that of Salcomine except that a slightly higher heating fluid temperature is required to give comparable desorption rates, since the ethoxy derivatives desorb at a higher temperature.

Interest in adiabatic units has been revived. A preliminary evaluation of the properties of the ethoxy derivative of Salcomine for adiabatic operation has been made and a similar evaluation of the methoxy derivative is in progress. The ethoxy derivative can be operated at around 90°C. using air at 150 to 250 p.s.i. for absorption, and desorbing at an absolute pressure of 4 - 8 p.s.i. The methoxy derivative has properties practically identical to those of the ethoxy with the exception that the necessary temperature region is around 55°C. instead of 90°C. It is very possible that the methoxy derivative will show superior life in adiabatic operation because of the lower temperature. At present the methoxy derivative is more available than the ethoxy but may require drying of the air used for absorption. A small adiabatic unit is under construction and life tests under conditions approximately adiabatic are being started. For these tests a mixture of eight parts by weight of precipitated copper powder and one part of the absorbent is caked and granulated and placed in the usual jacketed half-inch tube. There may be some advantage in not using any foreign heat capacity agent in the bed at all, by supplying an additionally large quantity of the chemical absorbent in place of the metallic powders, salts such as ammonium chloride, potassium acetate, etc., all of which have been investigated as heat absorbent agents. If no such heat absorbent agent is included, the weight and size of the reactors might be somewhat increased, but the time of the charge would be greatly lengthened. The purging of the generator in order to produce pure oxygen still remains as a major problem.

A recent study has been [illegible] inorganic regenerative absorbents for atmospheric oxygen and some pilot plant runs have been made upon the alkali [illegible] results indicated that the total weight [illegible] unit producing 1000 lb of oxygen [illegible] not including trailers. However [illegible] done and still in progress by the [illegible] inorganic systems, it is believed that [illegible] the NDRC oxygen program for developing such [illegible] and further work by NDRC is not contemplated.

Oxygen Producing Units

[illegible]

1263560

The testing and engineering of the 100 CFH aircraft chemical unit is being pushed and the ethoxy derivative of Salcomine is being groomed as a substitute of the methoxy derivative in this unit.

A number of difficulties have been encountered in the completion of the shipboard chemical units, chief among which have been leaks in the tapered seats. However, to date two reactors have been on the line, and production of 200 CFH of oxygen has been reached with a pressure of 75 p.s.i. and an airflow of only 4500 CFH instead of the designed figure of 6500 CFH. Utilities such as steam and air are delivered at too low a pressure, so that the required airflow and vacuum on the ejector could not be obtained, and, consequently, the purity of the product was poor. The driers have been in operation for some time, but a heat leak somewhat greater than expected has made it impossible to meet the calculated cycle time. However, test data obtained indicated that the drier could be decreased in size, consequently some additional insulation has been added inside of each drier, thus cutting down the heat leak. All four of the reactors should be on the test line by December 1st and it is expected that the 100 p.s.i. oxygen compressor will also be delivered about that time. The timer and all instruments have already been thoroughly tested.

In spite of the progress made to date on the portable chemical units, it has been decided to drop all further work on the units in order to devote the materials and efforts to the rapid completion of the mechanical portable units.

OXYGEN PRODUCTION BY MECHANICAL METHODS

Problem AC-12: The Manufacture of Oxygen while in Flight for Use of a Combat Crew.

Problem NA-111: Portable Unit for Supplying Oxygen.

Problem NS-115: The Development [illegible] for the Production of Liquid Oxygen [illegible]

Problem NS-116: Portable [illegible] and Cutting [illegible] Aircraft.

Problem CE-29: Field Generator [illegible]

Progress Report: [illegible]

Progress Report: [illegible]

1263561

Apparatus Study

The tests on the close crimp, steel packing have been completed and compared to those previously obtained on the wide crimp aluminum packing. The efficiency of the steel packing was slightly higher but the pressure drop was 14 to 17 inches as against 2 to 3 inches for the aluminum packing. The steel packing had 50% more surface and weighed about 4 times as much as the aluminum packing. Because of the importance of this regenerative program, arrangements have been made to test a generator packed with copper.

A small column was tested with various types of fibre glass wool, all of which proved to be inferior to the other types of packing such as shoe eyelet, Berl saddles, glass rings, etc. Tests on the large packed columns are about completed.

An interest in Stedman packing has been revived and it is planned to test this type further, both in the two-inch and in a six-inch size, which has been ordered but has not been received.

Comprehensive tests on the rotating equi-angular spiral-packing for rectification columns have been completed, and it is expected that a test column will be installed in a working unit for a further test in the near future.

Considerable data are reported for tests of the Keyes-Collins heat exchangers.

Oxygen Producing Units

Every effort is made to complete the low-pressure trailer-mounted mechanical unit by January 1st. Practically all of the material and equipment has been ordered. The trailers have been built and shipped. The assembly of the equipment will start as soon as the trailers have been received. It now appears that it will be necessary to supply a cooling system for the oil used in the Franklin engines and air compressor, and it is not known how much of a job this will be nor how much it will add to the weight and complexity of the unit. The structure of the regenerator for this unit is well under way.

The layout of the medium-pressure submarine pilot-plant unit is practically complete and most of the material has been ordered. It is contemplated that this unit will be equipped with a rectification tower packed with Berl saddles, whereas a Stedman packed column will be used for the low-pressure submarine pilot plant.

Preliminary layout for the low-pressure pilot plant is being made; the [illegible] packing has been [illegible] are now being made [illegible] of this packing.

1263562

The process design of a 400 CFH mechanical unit for plane transportation has been worked up and a preliminary layout of the main cold box was made. This box would contain the fractionating column, the reversing Collins exchangers, and the liquefier. It is estimated that the complete unit would weigh about 7000 lbs. if available equipment such as air compressor, oxygen compressor and expander were used.

Little additional work has been done on the proposed 1000 CFH trailer-mounted unit of improved design and smaller size. Investigation is also being made of the possibility of designing a more efficient unit, that is, one having a considerably higher yield of oxygen, but it is feared that the increase in bulk and weight will not be justified.

Work on the trailer-mounted unit to produce 85 lbs. of liquid oxygen per hour is progressing. Much of the equipment will be delivered during November and December. However, the two items, the engine and the air compressors, especially may cause serious delay in the completion of this unit. Complete details of the Lycoming model O-435-T engine has been received from the Ordnance Department. It would appear that this engine is ideal for the proposed unit, but there is considerable doubt as to whether or not such an engine can be obtained. It now appears that the air compressors cannot be supplied before January 15, and it is contemplated that necessary changes in the compressors' design will require considerable time after delivery.

The trailer was received for the 4000 CFH trailer-mounted unit and the assembly of the apparatus of the trailer has begun. All material on order has been received except the air compressor which is now promised for shipment on November 12th.

A completion and testing of this unit is most urgent inasmuch as the Engineer Board is holding up the decision for the mass production of their oxygen producing units until this unit is available for comparison. Inasmuch as this unit uses a well-known cycle and standard equipment, it is practically guaranteed in performance even before completion and testing.

The unit designed for air conditioning the submarine is in the assembly stage and will be especially prepared for extensive tests and taking data. The expectation is that within a matter of weeks it will be ready. It is now definitely planned to supply a barrel refrigerating unit for cooling in order to increase the production to 40 lbs. of liquid oxygen per hour.

The new Mond airplane unit has been designed and parts are being constructed. This unit is in addition to the remodeled Mond unit received from England and when completed will be tested in conjunction with that unit [illegible] this unit will be delayed pending completion of the submarine air conditioning unit.

1263563

The present schedule on the constructing and testing of Collins low-pressure 100 CFH unit at the Frigidaire Company called for two models of present design, and in the near future two additional models incorporating improvements suggested by the present working model, and at a somewhat later date two further models of ultimate design for large scale production. This work is progressing at the plants of the Frigidaire Company.

ENGINES AND COMPRESSORS

Problem Nos. NL-B-42; AC-12; NA-111; NS-115; NS-116; NS-117.

Several models of the Collins expander have been on test. After some difficulty with the valves and correction thereof, the efficiency was improved from 55% to about 70%. However, engineering difficulties still persist with the valves.

The detailing of the high level reciprocating expander for the high pressure submarine pilot plant is now complete and materials are being ordered. It has now been determined that a hydraulic brake will be used for loading this expander.

In order to meet the delivery date of January 15 on the low level expander, it will be necessary to substitute two or three of the small pilot type expanders for the four-cylinder unit. The unit which will be supplied, however, will be modified upon the experience gained on testing the three Collins models now in operation.

Tests on the 1700 CFM rotary low temperature expander have been most satisfactory at various rotational speeds and with warm air. Some problems of bearing lubrication have now been worked out. A maximum efficiency of 82% has been obtained but in actual operation there will be minor heat leaks through the supports and shafts, and is expected to give a net performance of about 80%. The loading device for the final unit is expected to be a direct current generator loaded with resistors. A preliminary test has been made on a small nozzle, one-third the size of those of the [illegible] machine, and they appear to give within 1% the performance of the large nozzles. This indicates that an expander of this type might be produced for the truck unit.

The rotary 200 CFM Lysholm type compressor is not yet complete because of difficulty in obtaining certain precision parts. The patterns for the high pressure cylinders required on the compressor of the high pressure submarine pilot plant [illegible] and it is hoped [illegible] cylinders [illegible] by early February. The compressor [illegible] the low pressure [illegible] the pilot plant [illegible] hoped will be [illegible]

1263564

The small, low pressure 150 p.s.i. engine compressor combination has been delayed because of difficulty encountered in the casting for cylinder heads. This equipment should be ready for test by the first of December.

The low pressure reciprocating air compressor for the 1000 CFH truck units is still under test. The unit operates very satisfactorily at the designed conditions. The capacity is actually about 95% of that estimated. Tests with the driving engine have been under way for long periods of time and it is considered that the unit is now ready for mounting with the rest of the equipment except for the trailer.

Although some more equipment has been obtained for the high pressure oxygen compressors, certain key parts have been held up so that the units are not yet ready for testing. It should be possible to begin tests of the 150 p.s.i. oxygen compressor around the end of November.

Mr. Wonley, of the Ricardo Company, England, has now arrived in this country and will assist with the tests of the Ricardo compressor as well as on other compressor and engine designs of NDRC.

UNDERWATER PROPULSION

Problem NL-B61 Operation of Diesel Engines on Recycled Fuel and Exhaust Gases.

Final Report closing out the work of Standard Oil Development Company is being prepared for release.

The W.H.T. program on the dispersion of exhaust gases is now completed except for the preparation of the final report.

MISCELLANEOUS

Problem [illegible] Development of an Instrument for the Measurement of Oxygen Partial Pressures.

Problem [illegible] Development of Oxygen Breathing Equipment and Associated Apparatus.

[illegible] Development of Oxygen Breathing Apparatus for use with Liquid Oxygen.

[illegible] Development of [illegible] Automatically [illegible] Oxygen Rebreather [illegible]

[illegible] Development of [illegible] and Sealing [illegible]

1263565

Problem CE-29: Field Generation of Oxygen Gas.

Tests have been made on a thermostated model Pauling oxygen meter which indicate a satisfactory control within a range of about 1°F. which is considered satisfactory for most meters. A new type of pole piece construction making possible an assembly which can be sealed up independently of the rest of the apparatus and giving an optical path which is less restricted by the pole pieces than in the standard design has been tried with promising results. Preliminary experiments on a new type of magnetic oxygen meter using an electro magnet excited by alternating current are being started. The development of a recording instrument is under way and it is expected that a working model will be ready by the end of the year.

Experiments have been made on a device which sounds the warning signal if the relative density of a gas passing through it exceeds a certain value. Such an apparatus will be useful in determining the concentration of air in hydrogen used as a filling for barrage balloons. The device is simple consisting of a pitch pipe connected to a glass tube about 44 cms. long producing a tone only when mixtures containing more than 21% air are present.

Small field generators for producing oxygen from sodium peroxide or potassium peroxide will be developed to form a supplementary supply of oxygen for the field treatment of gas casualties: shock, etc. It is contemplated that the generators will be small, light, and simple in operation, and that the peroxide may be furnished in small, convenient packages, which will be somewhat less in weight per oxygen produced than cylinders now used in the field. The development of such a generator is dictated primarily by the shortage of cylinders for field operations and the present lack of equipment for charging cylinders in the field. It may be that such a generator is of temporary importance only.

12635bb