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Div 11

Fifth and Final Progress Report

DEVELOPMENT OF
OXYGEN-CARRYING CHEMICALS

LISTED

1850

Contract OEMsr - 215
by
Harvey Diehl and Co-workers
at
Iowa State College

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Constituting
Oxygen Problem - Report LXXIX
Report No. 75 to the
National Defense Research Committee
Covering the Period
April 20, 1943 to June 30, 1943

No. 31

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1850

Division 11
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT.

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Final Report on "Development of Oxygen-Carrying Chemicals"
to
June 30, 1943
by
Harvey Diehl

Report OSRD No. 1850

Copy No. 31

Date: October 13, 1943

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Division 11
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT
Section 11.1

Final Report on "Development of Oxygen-Carrying Chemicals"
Service Directive NL-B42

Endorsement (1) From E. P. Stevenson, Chief, Division 11 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and noting:

"This is the final report in contract OEmr-215 reporting developments in the chemistry of regenerative oxygen carrying compounds of the chelate type. Of these, the original material "Salcomine" still appears to be the best all-purpose material, but other derivatives were found to have specific advantages. Engineering aspects of this type of oxygen-producing systems do not warrant further development of the chemistry of these compounds."

This is a final report under Contract 11-225, OEmr-215 with Iowa State College.

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This report is organized as a supplement to our previous Progress Reports (Reports XXVI, XLVI, LXXII and LXXIII); section numbers are therefore not consecutive, the same section number being reserved for the same subject matter. Inasmuch as the present report is also a final report the following Table of Contents has been compiled for all five Progress Reports; this will provide a survey of the work done on contract OEFAR-215 and will aid in locating all of the information on a particular phase of the work.

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This document contains information regarding the activities of the United States within the meaning of the Espionage Act, U.S.C. 1831 and 1832, and its transmission or disclosure to an unauthorized person is prohibited by law.

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I₅. General Statement Regarding Personnel,
Working Conditions and Related Activities.

During the period covered by this report the major part of the work described was carried out by Mr. Lawrence Liggett and Mr. Ross Curtis. The efforts of Mr. Clifford Hach and Mr. Carl Anderson during this period were devoted entirely to work on the circulating solid apparatus.

As might be expected, as the rather unsuccessful work on the chemical method of producing oxygen drew to its close, fewer contacts were made with the groups working on the problem in other laboratories. There were no visitors to this laboratory during the period of this report and the only contact with other parties was by Mr. Lawrence Liggett when he visited Mr. E. P. Stevenson and Mr. F. S. Bacon in Cambridge late in May while on a trip east in another connection.

The Iowa State College has continued to extend every facility to the furtherance of work on this contract and its administrative officers have been constant in their sympathy and encouragement. As this work draws to a close, a full measure of appreciation should be extended the Iowa State College for its assistance.

II₅. General Review and Objective

The general method of preparing reports in this laboratory was outlined in the corresponding section of our First Progress Report, Report XXVI. This method of preparing detailed reports covering the individual items of the research program and of preparing periodic reviews of the work as progress reports has been continued through to this the Fifth and Final Progress Report. These reports now number LXXIX. A table giving the number, authors, contents, periods covered and dates of these reports is given in Appendix I.

The work of this laboratory during the period covered by this report has been devoted principally to four lines of research. At considerable effort several hundred grams of di-(2-hydroxy-3-n-butoxybenzal)ethylenediimine cobalt

(Co-Ox SS), a material possessing the highest rate of oxygenation yet observed on any compound, was prepared and shipped to the M. I. T. laboratory for engineering and life studies. The search for new compounds was continued, efforts along this line being devoted to the testing of the compounds from numerous aldehydes derived from various commercially available phenols and to substituted acetophenone and propiophenone derivatives. An investigation into the possibility of finding a means of operating the oxygen-producing cycle in solution by dissolving the oxygen-carrying compounds in solutions of nitrogenous materials to produce a composition more closely resembling the hemoglobin of blood, the nitrogenous materials playing a role analogous to hemoglobin, was nicely under way at the termination of the contract. Work on the circulating-solid apparatus was continued during the period of this report; this work is covered in our Fourth Progress Report and will not be treated in this report.

III₅. General Summary

1. Several hundred grams of di-(2-hydroxy-n-butoxybenzal)-ethylonediamine (Co-Ox SS) were prepared and sent to the M. I. T. group for engineering and life studies. The yields of the intermediate products were considerably improved and a method was devised by which the cobalt compound could be produced having the theoretical capacity.
2. The following aldehydes were prepared by the application of the Duff reaction to the proper phenols:

2-hydroxy-3-iso-propyl-6-methylbenzaldehyde
2-hydroxy-3,5-dimethylbenzaldehyde
2-hydroxy-3,5-di-(tert-amyl)benzaldehyde
2-hydroxy-3-tert-amylbenzaldehyde
2-hydroxy-3-methyl-5-tert-amylbenzaldehyde
2-hydroxy-3-chloro-5-tert-butylbenzaldehyde
2-hydroxy-3-bromo-5-tert-butylbenzaldehyde
2-hydroxy-3-iso-propyl-5-chloro-6-methylbenzaldehyde
2-hydroxy-3,5-dibrombenzaldehyde
2-hydroxy-3-carboxybenzaldehyde

These aldehydes yielded yellow, highly crystalline Schiff's bases which in turn gave well defined cobalt derivatives. None of the cobalt compounds, however, carried

oxygen after having been heated in a vacuum at temperatures up to 170° (activation treatment) and subsequently subjected to an atmosphere of oxygen of 200 p.s.i.g.

3. The Duff reaction was applied to several phenols which would be expected to yield two ortho-hydroxy aldehydes. The yields were exceptionally high in these cases. Methods could possibly be devised for the separation of these aldehydes but it was considered hardly worth while for this problem. Although the aldehydes isolated and their derivatives possessed sharp melting points, it was felt unsafe to conclude that the products were individual compounds. These phenols and the expected products were:

4-hydroxy-1,2-dimethylbenzene
2-hydroxy-5,6-dimethylbenzaldehyde
2-hydroxy-4,5-dimethylbenzaldehyde

3-methyl-4-tert-butylphenol
2-hydroxy-4-methyl-5-tert-butylbenzaldehyde
2-hydroxy-4-tert-butyl-6-methylbenzaldehyde

2-hydroxy-4-tert-butylphenol
2,3-dihydroxy-5-tert-butylbenzaldehyde
2,3-dihydroxy-6-tert-butylbenzaldehyde

3-Methyl-4-chlorophenol
2-hydroxy-4-methyl-5-chlorobenzaldehyde
2-hydroxy-5-chloro-6-methylbenzaldehyde

The Schiff's base of each mixture and ethylenediamine was prepared and converted to the corresponding cobalt compound. None of the products carried oxygen.

4. The Duff and Reimer-Tiemann reactions failed on a number of phenols, notably on 2-hydroxy-3,5-dinitrobenzaldehyde, thiosalicylaldehyde, 2-hydroxypyridine, and 3,5-dinitro-o-cresol.
5. When properly prepared the cobalt compound of o-hydroxyacetophenone and ethylenediamine, di-(2-hydroxyacetophenone)-

ethylenediimine cobalt, was found to carry oxygen reversibly to the extent of about 4 per cent. The rate of oxygenation was very low, however, even under relatively high oxygen pressure. Since the introduction of a nitro or an alkoxy group into the 3- position of the parent compound, dialicylaethylenediimine cobalt, greatly increased the rate of oxygenation, a similar approach was indicated with *o*-hydroxyacetophenone. The corresponding 3-nitro compound was prepared but found to be inactive. Work was begun on the 3-methoxy compound but was incomplete when the work on this contract terminated. The cobalt compound from 2-hydroxy-5-methylacetophenone was found to be active but slow. The corresponding 4-methyl compound was inactive. 2-Hydroxypropiophenone was also investigated but, although a Schiff's base with ethylenediamine could be readily prepared, a cobalt compound could not be made.

6. Ethylene-bis-thioglycollic acid, $\text{HOOC-CH}_2\text{-S-CH}_2\text{-CH}_2\text{-S-CH}_2\text{-COOH}$, yielded a cobalt compound resembling the parent compound in general molecular structure. The compound did not carry oxygen, however.
7. A compound in which the double bond linkage of aldehyde to amino of the parent compound were hydrogenated would be of interest in being possibly less susceptible to oxidation and therefore of a longer useful life as an oxygen carrier. An attempt was made to prepare the hydrogenated parent compound by the condensation of salicyl alcohol and ethylenediamine. A resin was obtained which would not yield a cobalt derivative and it appears that some other approach will be required for the synthesis of the hydrogenated compound, dialicylaethylenediimine.
8. Following up earlier observations that the rate of oxygenation of the compounds under study in this laboratory was in some manner conditioned by the pretreatment the compounds had received, careful experimentation showed that the rate of oxygenation varied greatly during the first few cycles of oxygenation and deoxygenation. It is recommended that compounds be alternately oxygenated and deoxygenated four times just prior to a determination of their rate of oxygenation.
9. Reasoning by analogy with hemoglobin it appeared likely that dialicylaethylenediimine cobalt should be soluble in solutions of nitrogenous materials such as pyridine,

amino acids, and proteins and that such a solution should carry oxygen reversibly if adjusted to the proper value of pH. The operation of the oxygenation-dooxygenation cycle would be greatly simplified from an engineering standpoint if such a solution could be found. The solubilities of disalicylaldehydediimine cobalt and salicylaldehydediimine iron in solution of pyridine of different concentrations and different value of pH and in solutions of various other nitrogenous materials were under way when the work on this contract was concluded.

VI. Cobalt Compounds from Substituted Salicylaldehydes and Similar Carbonyl Compounds and Ethylenediamina

G. o-Hydroxyacetophenona

The earlier work with o-hydroxyacetophenone (First Progress Report, P. 31) was left rather incomplete. In view of the necessity of activating the type of materials under study before testing for oxygen absorption it was felt desirable to study the o-hydroxyacetophenone derivative further.

The o-hydroxyacetophenone used in this work was obtained in part from Eastman Kodak Company and in part by preparations carried out in this laboratory. The o-hydroxyacetophenone prepared in this laboratory was prepared by the Fries reaction on phenyl acetate. The compound di-(o-hydroxyacetopheno)ethylenediimine was prepared by the condensation of o-hydroxyacetophenone and ethylenediimine in absolute alcohol, m.p.: 195°. The compound di-(o-hydroxyacetopheno)ethylenediimine cobalt was prepared by dissolving the condensation product in 70 per cent alcohol and adding a hot aqueous solution of cobalt acetate. An orange-red precipitate formed immediately, was filtered, washed and dried at 100° in a vacuum. This compound was found to carry oxygen reversibly to the extent of 4 per cent but was quite slow at room temperature even under 200 p.s.i.g. oxygen.

It appeared feasible to speed up the oxygenation of this compound by the introduction of a nitro or a methoxy group in the 3- position just as with the parent compound; work in this direction is reported in Sections AV and AZ below.

Q₅. 2-Hydroxy-3-n-butoxybenzaldehyde

Earlier work on this aldehyde and its cobalt compound, an active material having a high rate of oxygenation and designated as Co-Ox SS (Co-Ox Super Speed), was reported in our Third Progress Report, p. 38. Several hundred grams of this material was prepared subsequent to the report. A yield of 31 per cent was obtained in the conversion of catechol to its mono-butyl ether in larger quantity. The aldehyde was synthesized by numerous repetitions of the Duff reaction using 25 g. portions of ether; yields of 16 per cent were realized, somewhat better than obtained by the Duff reaction in general. A systematic study of the methods of preparing the cobalt derivative, Co-Ox SS was made. The best preparations of the cobalt compound were made by dissolving the Schiff's base in alcohol and adding to it an aqueous solution of cobalt acetate so that the final alcohol concentration was about 40 per cent. The compound prepared by this method carried 3.3 per cent, the theoretical value being 3.42 per cent. Other methods of preparation yielded material of considerably lower capacity. The material formed from the dilute alcohol solution was a yellow hydrate very similar in appearance to the corresponding methoxy compound. Unlike the methoxy compound, however, the butoxy compound became active at a temperature of 100°. The deoxygenation temperature was found to be 80°. The rate of oxygenation of Co-Ox SS at various temperatures was determined and is reported in our Third Progress Report and in our Report LXXVII where other details of this work will also be found. Co-Ox SS oxygenated completely within one minute or less at all temperatures that were tried. A sample of 100 g. of Co-Ox SS was forwarded to Dr. Catterall through Dr. Bacon for engineering and life studies.

AN. 2-Hydroxy-5,6-dimethylbenzaldehyde and
2-Hydroxy-4,5-dimethylbenzaldehyde

The Duff reaction was applied to 4-hydroxy-1,2-dimethylbenzene giving a 45 per cent yield of a light crystalline aldehyde, m.p.: 69°. Probably this unusually high yield was the result of the formation of two o-hydroxyaldehydes, since this phenol has two open positions, ortho to the hydroxyl group. Several unsuccessful attempts were made to separate

these isomers. The Schiff's base of this mixture of aldehydes and ethylenediamine was prepared and the product recrystallized from *n*-propyl alcohol, m.p.: 212-214°. A cobalt compound of the above Schiff's base was prepared; it was found to be inactive as an oxygen carrier.

AO. 2-Hydroxy-3,5-dimethylbenzaldehyde

2-Hydroxy-3,5-dimethylbenzaldehyde was prepared by the Duff reaction on 2,4-dimethylphenol. A yield of 31 per cent was obtained. The product was a light yellow oil which crystallized upon cooling to 23°. The phenylhydrazone derivative was prepared and crystallized from dilute alcohol, m.p.: 103°. The oxime derivative was also prepared, m.p.: 133°; Famberger and Wieler, (J. prakt. Chem., [2], 53, 352) reported the melting point of the oxime derivative to be 138°. The aldehyde formed a Schiff's base with ethylenediamine, m.p.: 132.5°. The compound, di-(2-hydroxy-3,5-dimethylbenzal)ethylenediimine cobalt, was prepared. The compound was found to not absorb oxygen when subjected to the usual activation treatments and oxygenation tests.

AP. 2-Hydroxy-3-iso-propyl-6-methylbenzaldehyde

The aldehyde 2-hydroxy-3-iso-propyl-6-methylbenzaldehyde was obtained by the means of a Duff reaction on thymol (2-iso-propyl-5-methylphenol). A yield of 18 per cent was obtained in this reaction. The product, a yellow oil, was fractionated under diminished pressure, b.p.: 105°/5 mm., refractive index: 1.5506 (25°). The semicarbazone derivative was prepared, m.p.: 194°; Ball and Henry (J. Chem. Soc., 1923, 2215) have reported the semicarbazone derivative of the aldehyde to melt at 198°. The Schiff's base of this aldehyde was prepared and recrystallized from absolute alcohol, m.p.: 112-113°. The compound di-(2-hydroxy-3-iso-propyl-6-methylbenzal)ethylenediimine cobalt was prepared but found to be inactive toward oxygen.

AQ. 2-Hydroxy-3,5-di-(tert-amyl)benzaldehyde

Attempts to prepare this aldehyde by the Duff reaction on 2,4-diamylphenol yielded extremely small amounts of aldehyde. Only about 5 g. of product was obtained from four Duff reactions using 50 g. of the phenol in each. An attempt to purify this small amount of material by vacuum distillation was unsuccessful because of decomposition of the product. The work was abandoned as lacking promise.

AR. 2-Hydroxy-3-tert-amylbenzaldehyde

2-Hydroxy-3-tert-amylbenzaldehyde was prepared by means of the Duff reaction on 2-tert-amylphenol. A yield of 20 g. of the aldehyde was obtained from three Duff reactions using 50 g. of the phenol in each. The product was purified by vacuum distillation, b.p.: 104°/4 mm. The Schiff's base of this aldehyde with ethylenediamine was prepared and recrystallized from alcohol, m.p.: 109.5°. The compound di-(2-hydroxy-3-tert-amylbenzal)ethylenediimine cobalt was prepared but was found inactive toward oxygen after drying at 100° or upon heating in a vacuum at temperatures up to 170°.

AS. 2-Hydroxy-3-methyl-5-tert-amylbenzaldehyde

This aldehyde was obtained by the Duff reaction on 2-methyl-4-tert-amylphenol and a yield of 45 g. was obtained from four Duff reactions using 50 g. of phenol in each. The product was further purified by vacuum fractionation, b.p., 108-110°/1 mm. The aldehyde formed a Schiff's base with ethylenediamine. On recrystallization from absolute alcohol, the product melted at 90°. The cobalt compound was prepared but was not active toward oxygen after the usual activation treatments at temperatures up to 170° in a vacuum.

AT. Mixture of Aldehydes from 3-Methyl-
4-tert-butylphenol

From the Duff reaction on 300 g. of 3-methyl-4-tert-butylphenol 50 g. of product was obtained. It seems probable that two o-hydroxy aldehydes would be obtained from this phenol. No attempt was made to separate these aldehydes but the product was used as such in the preparation of a Schiff's base with ethylenediamine and a cobalt derivative of the base. The Schiff's base was recrystallized from alcohol, m.p.: 165°. The cobalt compound was prepared and heated in a vacuum at temperatures from 100 to 180°. The compound did not function as an oxygen carrier.

AU. 2-Hydroxy-3-chloro-5-tert-butylbenzaldehyde

A 30 per cent yield of 2-hydroxy-3-chloro-5-tert-butylbenzaldehyde was obtained by the Duff reaction on 2-chloro-4-tert-butylphenol. The aldehyde was a light crystalline material which crystallized readily from dilute alcohol, m.p.: 72°. A phenylhydrazone derivative was prepared and recrystallized from alcohol, m.p.: 146°. The Schiff's base with ethylenediamine was prepared by condensation in alcohol solution. The melting point of the recrystallized product was 115°. A cobalt compound was prepared and found not to carry oxygen when subjected to the usual tests. The fact that this compound did not function as an oxygen carrier was disappointing inasmuch as the similar compound, di-(2-hydroxy-3-chlorobenzal)ethylenediamine cobalt previously prepared by Curtis, Report LXX, Part IV, Section B, page 7, had been found to carry oxygen. The explanation undoubtedly lies in the steric effect of the tert-butyl group. It has been shown in other sections of the present report and in previous reports, that aldehydes with more than one alkyl group or with groups larger than ethyl do not yield cobalt derivatives which are active toward oxygen.

AV. 2-Hydroxy-3-bromo-5-tert-butylbenzaldehyde

This aldehyde was obtained in 24 per cent yield by the Duff reaction on 2-bromo-4-tert-butylphenol. The aldehyde was recrystallized from dilute alcohol, m.p.: 88°. The phenylhydrazone and oxime derivatives were prepared. A melting point of the phenylhydrazone derivative was 143-144°, and that of the oxime derivative 169°. Dains and Pothrock (Am., 16, 644) have reported the melting point of this aldehyde to be 87° and of its oxime derivative 164°. The Schiff's base of this aldehyde was prepared by condensation in alcohol solution, m.p.: 120°. The compound, di-(2-hydroxy-3-bromo-5-tert-butylbenzal)ethylenediimine cobalt was prepared and subjected to the usual tests, but was found to be inactive as an oxygen carrier. This was as expected inasmuch as the corresponding chloro compound, di-(2-hydroxy-3-chloro-5-tert-butylbenzal)ethylenediimine cobalt, Section Au above, was found to be inactive.

AW. 2-Hydroxy-3-iso-propyl-5-chloro-6-methylbenzaldehyde

This aldehyde was prepared by the Duff reaction on p-chlorothymol. A yield of 12 g. of product from 100 g. of the phenol was obtained. The aldehyde was recrystallized from alcohol, m.p.: 49°. The oxime derivative was prepared, m.p.: 150-151°. The Schiff's base of this aldehyde and ethylenediimine was prepared by condensation in alcohol solution. Melting point of the recrystallized Schiff's base was 171°. The cobalt derivative was prepared and subjected to the usual tests but was found not to be active as an oxygen carrier.

AX. Mixture of Aldehydes from 2-Hydroxy-4-tert-butylphenol

The Duff reaction was run on p-tert-butyl catechol (2-hydroxy-4-tert-butylphenol). A yield of 31 g. of crude aldehyde was obtained from 100 g. of the phenol. The material was recrystallized from alcohol, m.p.: 85°. It is possible that this product was composed of two hydroxy aldehydes, i.e., 2,3-dihydroxy-5-tert-butylbenzaldehyde

and 2,3-dihydroxy-6-tert-butylbenzaldehyde. No attempt was made to separate the possible isomers but a phenylhydrazone derivative of the recrystallized product was prepared, m.p.: 160-161°. This material readily condensed with ethylenediamine in alcohol solution to give a yellow Schiff's base. The condensation product was recrystallized from alcohol, m.p.: 226°. The cobalt derivative of the Schiff's base was prepared and subjected to the usual tests. It was found to be inactive toward oxygen. The presence of two hydroxyl groups in the molecule made the cobalt compound more sensitive to oxidation since it was found that exposure of the hot cobalt compound (175°) to air caused it to ignite spontaneously and burn.

AY. 2-Hydroxy-3-nitroacetophenone

As reported on p. 5, the cobalt derivative of o-hydroxyacetophenone and ethylenediamine is active but absorbs oxygen slowly. Inasmuch as the introduction of a nitro group into the 3-position of salicylaldehyde gave a cobalt compound of greatly accelerated rate of oxygenation, it appeared likely that the 3-nitro derivative of o-hydroxyacetophenone might also yield a fast cobalt compound.

2-Hydroxy-3-nitroacetophenone was prepared by the direct nitration of o-hydroxyacetophenone in glacial acetic acid with concentrated nitric acid. The yield was exceptionally poor and various modifications of the original procedure were made in an effort to increase the yield. Following the nitration proper, the diluted reaction mixture was steam distilled to separate the nitrated phenone. It was thought the oxidation by the dilute nitric acid was responsible for the decreased yield and in one modification the acids were completely neutralized, the separated material extracted with ether and then steam distilled; the yield was no better.

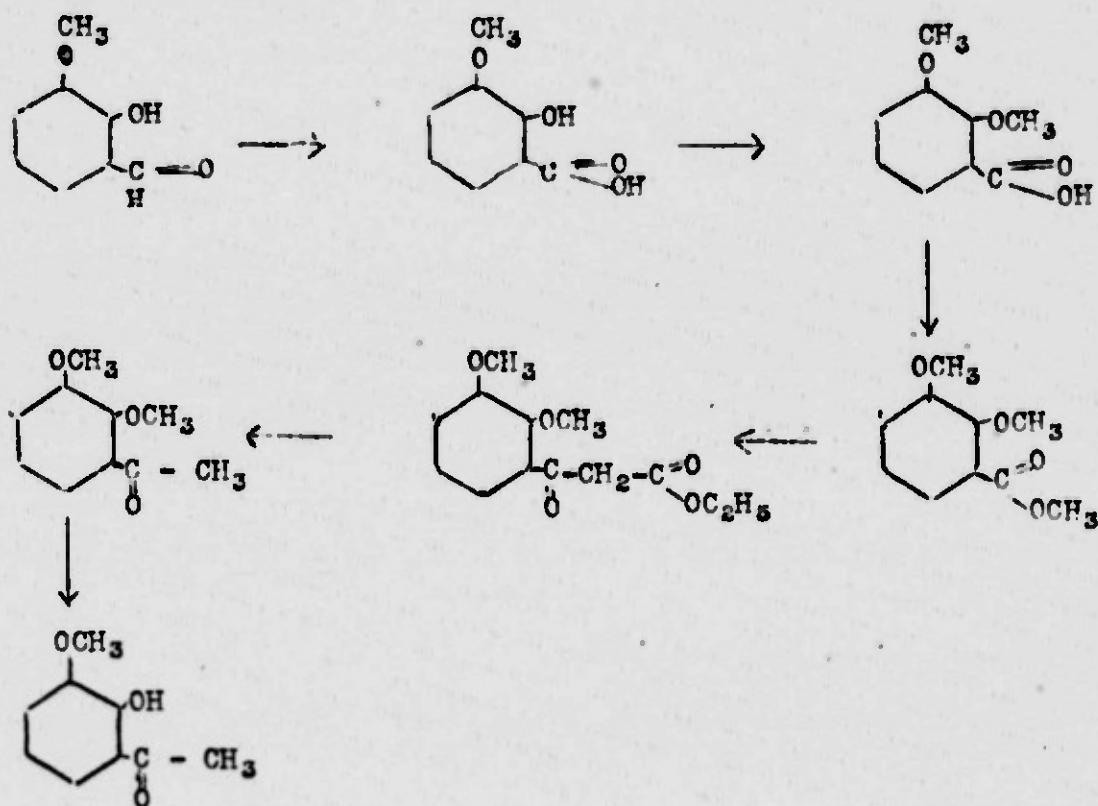
The 2-hydroxy-3-nitroacetophenone was obtained as white needles having a barely perceptible tinge of yellow; m.p.: 97-98° (reported 98.5-99.5°). The Schiff's base of 2-hydroxy-3-nitroacetophenone was formed by refluxing it in alcohol with an equivalent amount of ethylenediamine. A quantitative yield of a yellow base was obtained; m.p.: above 215°. Because of the insolubility of the Schiff's base in alcohol and water it was necessary to form the

cobalt derivative by triturating the base with a solution of the necessary amount of cobalt acetate and warming the suspension for some time. A dark red, insoluble material was obtained which was apparently the compound desired. It did not carry oxygen after drying at 100° or at higher temperatures.

AZ. 2-Hydroxy-3-methoxyacetophenone

Since the cobalt derivative of 2-hydroxy-3-methoxybenzaldehyde and ethylenediamine possessed a much higher rate of oxygenation than the corresponding salicylaldehyde compound (parent compound), it appeared possible that the cobalt derivative of 2-hydroxy-3-methoxyacetophenone would have a higher rate than that from 2-hydroxyacetophenone which has been shown to be active but slow.

The following synthesis of 2-hydroxy-3-methoxyacetophenone was proposed:



The first step in this process, the conversion of 2-hydroxy-3-methoxybenzaldehyde to 2-hydroxy-3-methoxybenzoic acid was carried out by fusing the aldehyde with potassium hydroxide at 210° for 10 minutes. The proper conditions were found after several tries and a final yield of over 90 per cent was obtained. 2-Hydroxy-3-methoxybenzoic acid is a white crystalline material melting at 148-149°.

2-Hydroxy-3-methoxybenzoic acid was converted to 2,3-dimethoxybenzoic acid by methylation with dimethylsulfate in sodium hydroxide solution. On acidification, the dimethoxybenzoic acid was obtained as white crystals, melting at 121-122°.

2-Hydroxy-3-methoxybenzoic acid was converted to its methyl ester by treatment with absolute methyl alcohol and dry hydrogen chloride. After the usual steps of dilution, extraction and washing, careful fractionation yielded material boiling 124-125°/2 mm.

Work on the next step of this synthesis was underway when the work on this contract ended.

BA. Mixtures of Aldehydes from 3-Methyl-4-chlorophenol

The Duff reaction was run on a 100 g. sample of 3-methyl-4-chlorophenol; a yield of 36 g. of crude product was obtained. The product which was a solid was recrystallized from 50 per cent alcohol, m.p.: 99°. The phenylhydrazones and oxime derivatives were prepared, melting at 205° and 131-132° respectively. The Schiff's base of this aldehyde with ethylenediamine was prepared and recrystallized from alcohol, m.p.: 221°. The cobalt compound was prepared by dissolving the Schiff's base in alcohol and adding an aqueous solution of cobalt acetate so that the final alcohol concentration was 40 per cent. The compound was subjected to the usual tests and found to be inactive.

BB. 2-Hydroxy-3,5-dinitrobenzaldehyde

An attempt was made to prepare 2-hydroxy-3,5-dinitrobenzaldehyde by the Duff reaction on 2,4-dinitrophenol. The product obtained on working up the reaction mixture in the usual manner was shown not to be the desired aldehyde but merely some of the original phenol. It was concluded that the Duff reaction does not proceed normally on a phenol having two nitro groups. This phenol is sufficiently acidic to form salts with ethylenediamine and phenylhydrazine. No further attempt was made to prepare this aldehyde by other means.

BC. Thiosalicylaldehyde

An attempt was made to prepare thiosalicylaldehyde by the Duff reaction on thiophenol. A crystalline product was obtained in very small yield. Upon recrystallization from dilute alcohol pure white crystals were obtained, m.p.: 60°. The product, however, did not react with ethylenediamine or with phenylhydrazine. The desired aldehyde had not been obtained and no further efforts to prepare it by this reaction were made.

BD. 2-Hydroxy-3-aldehydopyridine

Several attempts were made to prepare 2-hydroxy-3-aldehydopyridine by the application of the Duff reaction to 2-hydroxypyridine. The procedure was modified in a number of respects but none of the products isolated reacted with ethylenediamine or phenylhydrazine and it was concluded that no aldehyde had been obtained. Other methods of synthesizing 2-hydroxy-3-aldehydopyridine were devised and the synthesis by one of the proposed methods was under way when the work on this project terminated.

BE. 2-Hydroxy-3-methyl-4,6-dinitrobenzaldehyde

An attempt was made to prepare 2-hydroxy-3-methyl-4,6-dinitrobenzaldehyde by the Duff reaction on 3,5-dinitro-*o*-cresol. As in the case of the Duff reaction on 2,4-dinitrophenol reported in Section BE above, no aldehyde was obtained. Only a small amount of the original phenol was recovered from the reaction.

BF. 2-Hydroxy-4-methylacetophenone

About 100 g. of 2-hydroxy-4-methylacetophenone was prepared by the Fries reaction on *m*-cresyl acetate. The *m*-cresyl acetate was prepared from *m*-cresol and glacial acetic acid using acetyl chloride as the esterifying agent. The details of this preparation may be found in Report LXVII, Section III, Subsection C. The 2-hydroxy-4-methylacetophenone obtained was condensed with ethylenediamine and the condensation product recrystallized from *n*-propyl alcohol, m.p.: 223°. The cobalt compound was prepared by adding an aqueous solution of cobalt acetate to a hot solution of the condensation product in *n*-propyl alcohol. A brown compound was obtained which was subjected to the usual tests and found to be inactive toward oxygen.

BG. 2-Hydroxy-5-methylacetophenone

2-Hydroxy-5-methylacetophenone was prepared by the Fries reaction on *para*-cresyl acetate. The details of this preparation are described in Report LXVII, Section III, Subsection B. The acetophenone was obtained in a 73 per cent yield and had a crystallization point of 45°. The condensation product of this acetophenone and ethylenediamine was prepared. The reaction was carried out in alcohol solution and found to be slow as compared with the formation of Schiff's bases with *o*-hydroxy aldehydes. A small amount of the condensation product was recrystallized from 95 per cent alcohol, m.p.: 198°. The compound di-(2-hydroxy-5-methylacetophenone)ethylenediamine cobalt was prepared by

dissolving the condensation product in alcohol and adding to it a hot aqueous solution of cobalt acetate. The cobalt compound which was red in color formed immediately. The compound was dried in a vacuum at 100°. Upon heating this compound in a vacuum at temperatures of 130° and 175° only a very small additional loss in weight was observed. Upon exposure to oxygen at 200 p.s.i.g. the sample gained 1 per cent in weight. This gain in weight was observed upon exposure to 200 p.s.i.g. oxygen following activation in a vacuum at 100°, 130° and 175°. There was no change in color upon oxygenation as usually observed with other oxygen-carrying compounds. The compound did not appear to be appreciably hygroscopic since the weight remained constant upon standing in the balance case exposed to the atmosphere. In view of the above results further studies on this compound will be necessary to more fully ascertain its properties as an oxygen-carrying compound.

BH. 2-Hydroxy-3,5-dibromobenzaldehyde

From the Duff reaction on 100 g. of 2,4-dibromophenol there was obtained 7.5 g. of 2-hydroxy-3,5-dibromobenzaldehyde. The aldehyde was recrystallized from dilute alcohol, m.p.: 77°. The phenylhydrazone derivative of this aldehyde was prepared and recrystallized from alcohol, m.p.: 144-142°. The aldehyde was condensed with ethylenediamine in absolute alcohol, readily forming a very insoluble Schiff's base. A portion of the Schiff's base was recrystallized from *n*-propyl alcohol, m.p.: 247°. The compound di-(2-hydroxy-3,5-dibromobenzal)ethylenediimine cobalt was prepared by dissolving the Schiff's base in *n*-propyl alcohol and adding a hot aqueous solution of cobalt acetate. A dark brown compound was formed which was dried at 100° in a vacuum and subjected to the usual tests for oxygen capacity. The compound was not active towards oxygen.

BI. 2-Hydroxypropiophenone

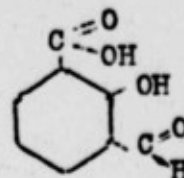
2-Hydroxypropiophenone was prepared by the Fries reaction on phenyl propionate. The phenyl propionate was prepared from phenol and propionic acid using thionyl chloride as the

esterifying agent. The Fries reaction on the ester was carried out by the procedure described in Organic Synthesis, Vol. XIII, p. 91. The condensation product of 2-hydroxypropionophenone and ethylenediamine was prepared and recrystallized from alcohol, m.p.: 118-118.5°. Several attempts were made using various methods to prepare the cobalt derivative but a solid cobalt compound could not be prepared.

BJ. 2-Hydroxy-3-carboxybenzaldehyde

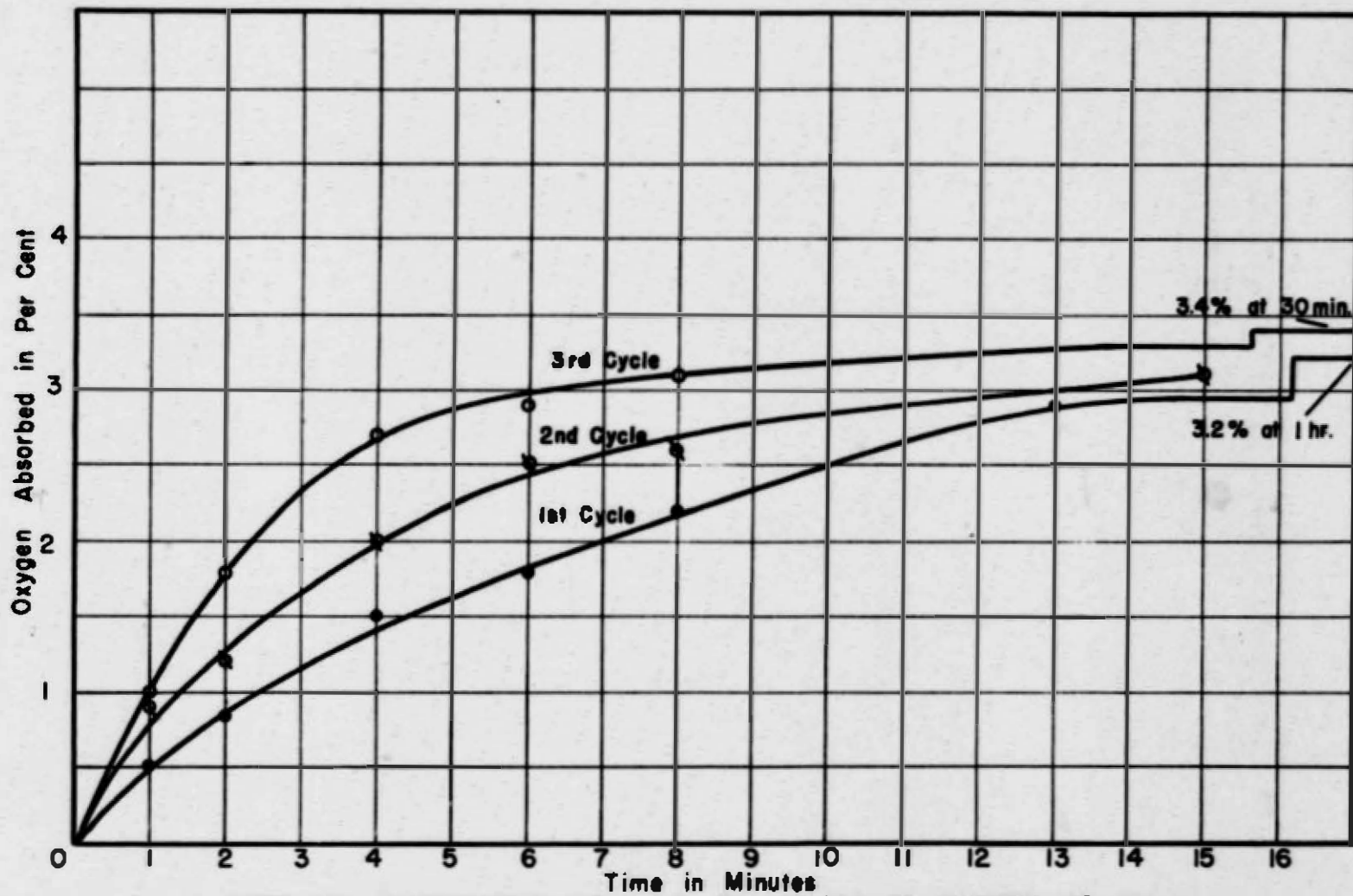
2-Hydroxy-3-carboxybenzaldehyde was first prepared by Reimer and Tiemann by the application of the Reimer-Tiemann reaction to salicylic acid. The synthesis of this compound was carried out in this laboratory with two purposes in mind.

First the 2-hydroxy-3-carboxybenzaldehyde itself should form a Schiff's base with ethylenediamine and this in turn a cobalt compound of interest as a possible oxygen carrier. Second, it was proposed to apply the Reimer-Tiemann reaction to 2-hydroxyphenylpropionic acid to obtain 2-hydroxy-3-aldehyde-phenylpropionic acid (Section XIII, below) and it appeared desirable to obtain experience with the application of this reaction to a similar, known product. Two aldehydes are produced by the Reimer-Tiemann reaction on salicylic acid. The involved procedure used by Reimer and Tiemann for the separation of these aldehydes was considerably simplified in this work by the direct precipitation of the copper salt of the desired ortho-aldehyde from which the aldehyde was subsequently recovered by treatment with acid. The yield was very poor.



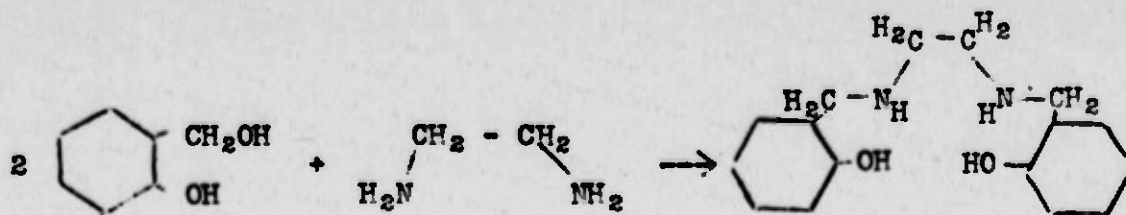
Several attempts were made to convert salicylic acid to 2-hydroxy-3-carboxybenzaldehyde by the Duff reaction but the results were uniformly unsuccessful.

A yellow insoluble material was formed on mixing 3-carboxysalicylaldehyde with ethylenediamine in alcohol. This material did not melt at temperatures up to 250°. It is assumed that this material was the desired Schiff's base but the possibility is not excluded that it was simply the ethylenediamine salt of 2-hydroxy-3-carboxybenzaldehyde. On treatment with a cobalt salt under the usual condition for the formation of a cobalt derivative of a Schiff's base, slimy,



RATE OF OXYGENATION OF Co-Ox BT AT 0°C. IN OXYGEN AT 71 cm.

carry oxygen. A direct synthesis of the organic portion of the desired compound appeared possible by the condensation of salicyl alcohol with ethylenediamine:



It was found that salicyl alcohol and ethylenediamine did not react until heated to 150°; reaction then occurred with the formation of an amber-colored resin. The resin was soluble in alkali, gave an orange color with ferric chloride but did not yield a cobalt derivative.

This approach to the problem of eliminating the double bond linkage of the parent compound appeared to lack promise and was abandoned.

X. Testing Apparatus

C. Apparatus for the Determination of the Rate of Oxygenation

(7) Variation of Rate of Oxygenation with Number of Cycles

It had been observed in this laboratory on a number of occasions that the rate of oxygenation of the type of oxygen carrying compounds under study varies with the pretreatment accorded the material. In an effort to secure more positive information on this point, it was discovered that the rate of oxygenation changed markedly during the first few cycles of oxygenation and deoxygenation.

A sample of di-(2-hydroxy-3-ethoxybenzal)ethylenediamine cobalt (Co-Ox BT) was prepared from purified 2-hydroxy-3-ethoxybenzaldehyde and nickel and iron free cobalt, the synthesis being carried out under the most ideal conditions.

A sample was activated at 100° in a vacuum and its rate of oxygenation determined in the simple manometric apparatus (Third Progress Report, p. 48). The results are reported graphically in the accompanying figure. The time required to obtain 80 per cent saturation was 10 minutes on the first cycle, 6.5 minutes on the second cycle, 4.5 minutes on the third cycle and the same on following cycles. It appears, therefore, that oxygen-carrying materials should be put through at least three cycles prior to the determination of their rate of oxygenation.

XIII. Soluble Oxygen-Carrying Compounds.
Operation of the Oxygenation-Deoxygenation
Cycle in Solution. Relation of Disalicylal-
ethylenediimine Cobalt to Heme.

The studies on the preparation of oxygen using disalicylal-ethylenediimine cobalt reversibly have in the past been devoted principally to the operation of the process as a gas-solid reaction. From an engineering standpoint this is a particularly difficult problem. It would be far simpler if the process could be made to operate in solution. Part of the very early work of Chao and Diehl was devoted to an attempt to prepare an oxygen-carrying compound which would be soluble in a petroleum solvent having a low vapor pressure. These early investigations did not meet with success (see reports of Chao and Diehl). Further work along this line was carried out by Liggott using pyridine and chloroform as solvents. It was found that a pyridine solution of the compound carried oxygen reversibly for one cycle only, after which the solution was inactive. The chloroform solution did not carry oxygen even for one cycle. This work is described in our First Progress Report, p. 21 and in more detail in Report X.

Disalicylal-ethylenediimine cobalt resembles hemoglobin, or more particularly the heme portion of hemoglobin, in a number of respects. Both heme and disalicylal-ethylenediimine cobalt are quadridentate chelate ring compounds, although in the former the organic molecule completely surrounds the metal atom (iron) forming a closed system of four rings, while in the latter compound, although there are the same number of bonds attaching the metal atom to the organic molecule, only three rings are present. Both are

probably flat molecules, that is the metal and the organic portion of the molecule all lie in the same plane, although the present evidence for this in the case of disalicylal-ethylenediimine cobalt is not conclusive. Both carry oxygen reversibly although in different amounts, hemoglobin carrying one molecule of oxygen per iron atom, disalicylal-ethylenediimine carrying one half a molecule of oxygen per cobalt atom. Heme, detached from the globin of hemoglobin, is inactive toward oxygen. When dissolved in solutions of pyridine or other nitrogenous materials it becomes able to carry oxygen. This naturally leads to speculation as to the behavior of disalicylal-ethylenediimine cobalt under such conditions. Perhaps by supplying a globin or similar nitrogenous substance, disalicylal-ethylenediimine cobalt can be made to function in solution like hemoglobin. The experiments of Liggett mentioned above were not a good test of this since the solid pyridine addition compound of disalicylal-ethylenediimine cobalt is known to be inactive toward oxygen; on the other hand a dilute solution of pyridine and the cobalt compound might behave entirely differently. It is known that heme when dissolved in solutions of nitrogenous materials only functions as an oxygen carrier when the pH of the solution has a definite value, usually about 7. It would appear that this factor also must be carefully considered in efforts to find a means of operating the oxygen producing cycle of disalicylal-ethylenediimine cobalt in solution. The literature on the subject of the oxygen-carrying property of hemoglobin is, of course, very extensive; much of it is, however, devoted to the biological aspects of the problem and is not pertinent to our problem. Little is known of the nature of the linkage of heme to globin. Undoubtedly the principal attachment is through secondary valence linkages between the iron atom and the nitrogen atoms of the protein globin; the propionic acid and vinyl side chains of heme, however, might also be involved. It would appear worthy to introduce these side chains into the disalicylal-ethylenediimine cobalt molecule and to determine their effect on the solubility and stability of their solutions in solutions of nitrogen containing materials.

Following up these lines of thought suggested above, the solubility of disalicylal-ethylenediimine cobalt in various nitrogenous materials was determined. Table I summarizes these solubility studies. These studies were made by adding an excess of disalicylal-ethylenediimine cobalt to the solvent to be tested and stirring the mixture vigorously with a mechanically driven stirrer for sixty minutes. The excess cobalt compound was then removed by filtration

and a measured volume of the solution taken for analysis. The analysis was made by decomposing the organic material using nitric, sulfuric and perchloric acid mixture, the final analysis for cobalt being made colorimetrically.

A series of solubility determinations was made using concentrations of pyridine varying from 0.005 molar up to and including pure pyridine (I - VI in Table I). The solubility was found to be a function of the pyridine concentration, the compound being soluble to the extent of 4:1 per cent in pure pyridine. The solubility in 50 per cent pyridine was of such an order that assuming the cobalt compound to be active the solution would carry a far greater percentage of oxygen than blood. The solubility of the compound in pure water was found to be very low and is included in the Table (X) for purposes of comparison.

The solubility of the compound in 50 per cent pyridine solutions of various pH values was determined (Table I, XI - XV). The pyridine solutions were buffered to the desired pH values by the addition of hydrogen chloride and water. All solutions contain a total of 50 per cent pyridine in the form of free pyridine and pyridine hydrochloride. The solubility of the compound in these various solutions was approximately the same except with pH values of 2 or below in which the material was decomposed because of the high acidity.

The solubility was also determined in aqueous solutions containing egg albumen and glycine, (VII - IX). These materials exert negligible solvent power.

From the above solubility studies no decisive conclusions may be drawn. It was only hoped that some insight into the problem might be obtained which would indicate the lines along which further research should follow.

Inasmuch as hemoglobin contains iron as the metal in this metal-organic molecule an analogy with this cobalt compound may not be justifiable in every case. For purposes of comparison the solubility of disalicylalathylene-diamine iron in various nitrogen containing solvents has also been determined. These results are summarized in Table II. These solubility studies were carried out in the manner described above for the cobalt compound. The iron was determined following decomposition of the organic material with nitric-perchloric-sulfuric acid mixture by reduction with aluminum wire followed by titration with

potassium permanganate. In general it was found that the iron compound was somewhat less soluble than the cobalt compound.

The next step in this study consisted in the cyclic operation of these solutions at different pH. This study was under way when the work on the contract at Iowa State College ended.

TABLE I.

Solubility Studies on Disalicylaethylenediimine Cobalt in Various Solvents

No.	Nature of Solvent	Initial pH	Final pH	Cobalt g./100 ml.	Disalicylaethylene- diimine Cobalt gram/100 ml.
I	Pure Pyridine.	--	--	0.74	4.1
II	Pyridine, 1 Molar, buffered.	7.1	7.4	0.072	0.39
III	Pyridine, 0.1 Molar, unbuffered.	8.6	10.7	0.0475	0.26
IV	Pyridine, 0.02 Molar, unbuffered.	7.6	--	0.021	0.12
V	Pyridine, 0.01 Molar, unbuffered.	7.6	--	0.028	0.15
VI	Pyridine, 0.005 Molar, unbuffered.	7.6	--	0.012	0.067
VII	Pyridine, 0.1 Molar. Egg albumen added.	7.5	9.5	0.034	0.19
VIII	Solution of Egg albumen in water.	6.5	--	0.011	0.062
IX	Glycine, 1 per cent buffered.	6.9	6.9	0.019	0.10
X	Pure water.	6.7	7.7	0.0035	0.019
XI	Pyridine 50 per cent, buffered.	2.0	--	Decomposed	
XII	Pyridine 50 per cent, buffered.	4.0	4.5	1.04	5.9
XIII	Pyridine 50 per cent, buffered.	5.9	6.0	0.82	4.7
XIV	Pyridine 50 per cent, buffered.	7.2	10.0	0.82	4.7
XV	Pyridine 50 per cent, unbuffered.	9.6	13.0	0.82	4.7

TABLE II

Solubility of Disalicylaethylenediimine Iron in Various Solvents

No.	Nature of Solvent	Initial pH	Final pH	Iron g./100 ml.	Disalicylaethyl-enediimine Iron grams/100 ml.
I	Pyridine 50 per cent, buffered.	2.45	2.85	0.088	0.5192
II	Pyridine 50 per cent, buffered.	5.7	5.3	0.485	2.86
III	Pyridine 50 per cent, buffered.	6.5	6.0	0.210	1.23
IV	Pyridine 50 per cent, buffered.	6.9	6.95	0.083	0.489
V	Pure Water.	—	--	0.0044	0.025
VI	Ethylenediamine, pure.	--		Slightly soluble	--
VII	Ethylenediamine, 10 per cent in water.	--		Slightly soluble	--
VIII	Glycine, 10 per cent in Water.	6.2	5.9	0.074	0.44
IX	Glycine, 25 per cent in Water.	5.2	5.7	0.096	0.566
X	Quinoline.			Slightly soluble	

APPENDIX I.

SUMMARY OF REPORTS ON OXYGEN PROBLEM

<u>Report No.</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
Chao 1		Chao and Diehl		10-20-38
	Cobalt, iron and manganese derivatives of disalicylalathylenediimina; disalicylalbenzidina cobalt; test for oxygenation capacity; luminescence test.			
Chao 2		Chao and Diehl		11-20-38
	Cobalt, iron, cooper, and chromium derivatives of disalicylalethylenediimine; cobalt, iron, and manganese derivatives of disalicylalphenylenediimina; cobalt, iron and manganese derivatives of disalicylalbenzidine.			
Chao 3		Chao and Diehl		12-20-38
	Tin derivatives of disalicylalethylenediimina and disalicylalphenylenediimine; lead disalicylalethylenediimine; effect of nitrogen on disalicylalethylenediimine cobalt; salicylalamide cobalt.			
Chao 4-5		Chao and Diehl		3-3-39
	Reduction of nitroalkanes; purification of salicylaldehyde; Schiff's bases of salicylaldehyde and various alkylamines; cobalt derivatives of the latter; preparation of disalicylalethylenediimine cobalt of high capacity.			
Chao 6-7		Chao and Diehl		4-28-39
	Continuation of work on derivatives of monamines with salicylaldehyde and ammonia; methylamine, ethylamine, <u>n</u> -propylamine, <u>iso</u> -propylamine, <u>n</u> -butylamine, <u>n</u> -amylamine, aniline.			
I		Hach and Diehl	10-1-40 to 2-15-41	2-17-41
	Constitution of disalicylalethylenediimine cobalt; analysis and molecular weight of disalicylalethylenediimine cobalt; the effect of light on the material; the effect of pressure on oxygenation; apparatus for producing oxygen; preparation; di-			

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
			(3-nitrosalicylal)ethylenediimine cobalt; di-(5-nitrosalicylal)ethylenediimine cobalt; cobalt derivatives of salicylaldehyde and diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and hydroxyethylethylenediamine; mechanism of the oxygenation process.	
II		Hach and Diehl	2-15-41 to 3-15-41	3-19-41
			Effect of light of various wave lengths on disalicylaethylenediimine cobalt; temperature of deoxygenation; study of synthesis and olive, red, and black by-products; other methods of preparation; presence of water in the compound; the valence of cobalt in the compound; the rate of oxygenation.	
III		Diehl, Hach and Harrison	3-15-41 to 8-25-41	8-27-41
			The rate of oxygenation of disalicylaethylenediimine cobalt at different temperatures and pressures; construction of apparatus; continuous, circulating-solid apparatus, batch operation without stirring (stationary head) with and without recirculation of gases, batch process with stirring using paddle and using rotating drum; explosibility; density; further notes on preparation of large batches; the effect of moisture.	
IV		Diehl, Hach and Harrison	8-25-41 to 11-10-41	11-14-41
			Preparation of disalicylaethylenediimine cobalt; the various methods; effect of the purity of the salicylaldehyde, effect of excess of any one of the reactants, effect of the order and rate of addition of reagents, effect of temperature, effect of alcohol concentration, effect of volume of solvent, effect of cooling; effect of composition of wash liquid; effect of washing; effect of manner of drying; recommended procedures.	

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
V	1	Hach, Harrison and Diehl	11-10-41 to 1-5-42	1-8-42
			Further studies on preparation of disalicyl- ethylenediimine cobalt; Harrison-Hach method; direct mixing method; analysis of disalicyl- ethylenediimine cobalt; high temperature drying; dirty brown compound; bright red inactive com- pound; stereochemical considerations; effect of washing with alcohol and benzene; effect of car- bon monoxide, nitric oxide, nitrogen dioxide; the recovery of salicylaldehyde and cobalt.	
VI	2	Henselmeier and Diehl	12-15-41 to 1-2-42	1-7-42
			Ethylenediimine, pyruvic acid and cobalt.	
VII	3	Diehl	1-10-42 to 2-14-42	2-14-42
			Monthly report.	
VIII	4	Harrison and Diehl	1-5-42 to 1-15-42	2-23-42
			Disalicylalpropylenediimine cobalt.	
IX	5	Hach and Diehl	1-42	2-23-42
			Effect of nitrogen dioxide, nitrous oxide, and sulfur dioxide on disalicylaethylenediimine, disalicylaethylenediimine cobalt, and the bright red inactive isomer.	
X	6	Liggett and Diehl	12-15-41 to 1-20-42	2-23-42
			Preparation of disalicylaethylenediimine co- balt by pyridine method; cobalt and iron deriv- atives of disalicylalphenylenediimine; opera- tion of disalicyloethylenediimine cobalt in solution in pyridine and in chloroform.	
XI	7	Head and Diehl	12-15-41 to 1-23-42	2-23-42
			Tridentate cobalt compounds from <u>o</u> -hydroxy- benzalimino- <u>o</u> -phenol.	

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
XII	8	Diehl	2-14-42 to 3-14-42	3-14-42
			Monthly report.	
XIII	9	Henselmeier and Diehl	1-2-42 to 2-14-42	3-9-42
			Cobalt derivatives of pyruvic acid and ethylenediamine, propylenediamine, and <i>o</i> -phenylenediamine.	
XIV	10	Hech and Diehl	2-18-42 to 3-24-42	4-14-42
			Nitration of salicylaldehyde; separation of 3- and 5-nitro isomers; di-(3-nitrosalicylal)-ethylenediamine cobalt; di-(5-nitrosalicylal)-ethylenediamine cobalt.	
XV	11	Head and Diehl	4-6-42 to 4-9-42	4-14-42
			Nitration of salicylaldehyde: variation in nitric acid concentration.	
XVI	12	Liggett and Diehl	1-17-42 to 3-25-42	3-27-42
			3-, 4-, 5-, and 6-methylsalicylaldehydes, their condensation with ethylenediamine and cobalt; di-(2-hydroxy-3-methoxybenzal)ethylenediamine cobalt; 2-hydroxy-1-naphthaldehyde and its condensation with ethylenediamine and cobalt; study of Reimer-Tiemann reaction.	
XVII	13	Henselmeier and Diehl	2-14-42 to 3-3-42	4-27-42
			Disalicylaldehydene ethylenediamine cobalt by pyridine method; disalicylalpropylenediamine cobalt by pyridine method; <i>o</i> -hydroxyacetone with ethylenediamine and cobalt; resacetophenone; di-(2-hydroxy-3-methoxybenzal)-ethylenediamine cobalt.	

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
XVIII	14	Head and Diehl	2-20-42 to 3-4-42	3-16-42
			Resolution of propylenediamine end disalicylal-1-propylenediimine cobalt.	
XIX	15	Head and Diehl	1-31-42 to 2-10-42	4-14-42
			Disalicylaethylenediimine iron.	
XX	16	Harrison and Diehl	1-1-42 to 2-24-42	
			The magnetic susceptibility of disalicylal-ethylenediimine cobalt and related compounds.	
XXI	17	Head, Hach and Diehl	2-20-42 to 3-2-42	5-6-42
			Cobalt, salicylaldehyde and decamethylenediamine, nonamethylenediamine, hexamethylenediamine, trimethylenediamine, iso-propylamine, and 2,3-butylenediamine; preparation of disalicylaethylenediimine cobalt; density of disalicylaethylenediimine cobalt, cobaltinitrite method of purifying cobalt.	
XXII	18	Harrison and Diehl	2-19-42 to 2-20-42	4-27-42
			Cobalt, iron and manganese derivatives of ethylenediamine and 3-bromosalicylaldehyde.	
XXIII	19	Diehl	3-14-42 to 4-15-42	4-16-42
			Monthly report.	
XXIV	20	Harrison and Diehl	2-24-42 to 3-29-42	7-20-42
			Preparation of disalicylaethylenediimine cobalt under anhydrous conditions; the green and orange compounds and their conversion with water to oxygen carriers.	

<u>Report Number</u>	<u>Report to NDRG No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
XXV	21	Head and Diehl	3-22-42 to 3-26-42	5-1-42
			2-Hydroxy-3-methoxy-5-nitrobenzaldehyde and its condensation with ethylenediamine and cobalt.	
XXVI	22	Diehl	12-1-41 to 4-15-42	4-22-42
			First progress report.	
XXVII	23	Liggett and Diehl	3-26-42 to 5-13-42	5-13-42
			Di-(3-hydroxy-3-methoxybenzal) ethylenediamine cobalt' preparation by various methods' volumetric determination of oxygen capacity, rate of oxygenation.	
XXVIII	24	Diehl	4-15-42 to 5-13-42	5-13-42
			Monthly report.	
XXIX	25	Head and Diehl	4-17-42 to 5-15-42	9-21-42
			Nitration of salicylaldehyde; variation of excess nitric acid and of amount of acetic acid; recommended procedure.	
XXX	26	Hach, Head and Diehl		
			Rate of deterioration of disalicylaethylenediamine cobalt and di-(2-hydroxy-3-methoxybenzal) ethylenediamine cobalt with rotating drum machine.	
XXXI	27	Hach, Liggett and Diehl	3-15-42 to 9-7-42	9-23-42
			Di-(2-hydroxy-3-nitrobenzal) ethylenediamine cobalt activation, rate of oxygenation at various temperatures, pressures and humidities, rate of hydration and oxygenation.	

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
XXXII	28	Henselmeier and Diehl	4-1-42 to 5-15-42	7-15-42
			Di-(2-hydroxy-3-methoxybenzal) ethylenediimine cobalt' synthesis of 2-hydroxy-5-phenylbenzaldehyde by the Duff reaction; synthesis of 2-hydroxy-3-nitro-5-methylbenzaldehyde.	
XXXIII	29	Diehl	5-13-42 to 6-15-42	6-17-42
			Monthly report.	
XXXIV	30	Hach and Diehl	5-20-42 to 7-23-42	7-27-42
			Circulating solid apparatus.	
XXXV	31	Schwandt and Diehl	6-1-42 to 7-25-42	8-5-42
			Tetramethylethylenediamine with cobalt and salicylaldehyde, with 2-hydroxy-3-methoxybenzaldehyde, end with 2-hydroxy-3-nitrobenzaldehyde.	
XXXVI	32	Harrison and Diehl		
			Differential manometric capacity and rate apparatus; summary of applications.	
XXXVII	33	Brouns and Diehl	6-16-42 to 8-31-42	9-25-42
			Preparation of <u>o</u> -ethoxyphenol; preparation of 2-hydroxy-3-ethoxybenzaldehyde by the Duff reaction; di-(2-hydroxy-3-ethoxybenzal) ethylenediimine cobalt; preparation, activation, rate of oxygenation, hydration and dehydration; demethylation of 2-hydroxy-3-methoxybenzaldehyde; ethylation of 2,3-dihydroxybenzaldehyde; preparation of <u>o</u> - <u>n</u> -propoxyphenol; preparation of 2-hydroxy-3- <u>n</u> -propoxybenzaldehyde; di-(2-hydroxy-3- <u>n</u> -propoxybenzal) ethylenediimine cobalt.	

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
XXXVIII	34	Liggett, Head, Diehl, Calvin and Co-workers	5-13-42 to 7-24-42	7-24-42
		Di-(2-hydroxy-3-methoxybenzal) ethylenediimine cobalt: additional studies on methods of preparation, large scale preparation, activation apparatus, hygroscopicity and effect on capacity, analysis, magnetic susceptibility (Calvin), rate of oxygenation, rate of deterioration in use, equilibrium pressure (Calvin).		
XXXIX	35	Diehl	6-15-42 to 7-23-42	7-23-42
		Monthly report.		
XI	36	Diehl	7-24-42 to 8-15-42	8-15-42
		Monthly report.		
XLI	37	Head and Diehl	4-24-42 to 5-20-42	9-21-42
		2-Hydroxy-3-bromobenzaldehyde with ethylenediamine and cobalt.		
XLII	38	Harrison and Diehl	7-22-42 to 8-21-42	9-22-42
		2,3-Dihydroxybenzaldehyde with ethylenediamine and cobalt.		
XLIII	39	Mathews and Diehl		
		Acetylacetone, benzoylacetone, and dibenzoylmethane with ethylenediamine and cobalt.		
XIIV	40	Mathews and Diehl	5-1-42 to 6-1-42	9-14-42
		Allylamine polynuclear compounds.		

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
XLV	41	Liggett and Diehl	7-11-42 to 8-24-42	9-11-42
			2-Hydroxy-3-nitro-5-methylbenzaldehyde with ethylenediamine and cobalt; formylcamphor with cobalt and ethylenediamine and with <i>o</i> -phenylenediamine; methylenediamine with salicylaldehyde and cobalt.	
XLVI	42	Diehl	4-15-42 to 9-1-42	9-26-42
			Second progress report.	
XLVII	43	Heed and Diehl	3-22-42 to 3-8-43	3-11-43
			2,4-Dihydroxybenzaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2,5-dihydroxybenzaldehyde, 2-hydroxy-5-methoxybenzaldehyde, and 2-hydroxy-5-ethoxybenzaldehyde; their condensation with ethylenediamine and the cobalt derivatives.	
XLVIII	44	Harrison and Diehl	8-19-42 to 11-4-42	11-4-42
			3-Alkoxy compounds.	
IL	45	Diehl	8-15-42 to 9-15-42	9-15-42
			Monthly report.	
L	46	Haeh and Diehl	5-20-42 to 10-31-42	1-15-43
			Report No. 1 to NRL Circulating-solid apparatus, heat transfer studies, design of second model.	
LI	47	Brouns and Diehl	9-1-42 to 12-18-42	1-20-43
			Further studies on ethoxy compound, Co-Ox BT	

<u>Report Number</u>	<u>Report to NDRG No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
LII	48	Diehl	9-15-42 to 10-15-42	10-15-42
			Monthly report.	
LIII	49	Curtis and Diehl	10-26-42 to 10-29-42	1-26-43
			Attempts to activate inactive compounds by steam treatment.	
LIV	50	Harrison and Diehl	10-21-42 to 1-15-43	2-10-43
			Preparation and study of cobalt derivatives of mixtures of aldehydes.	
LV	51	Head, Liggett and Diehl	10-5-42 to 11-18-42	12-3-42
			Commercial preparation of 2-hydroxy-3-ethoxybenzaldehyde by Reimer-Tiemann reaction.	
LVI	52	Diehl	10-15-42 to 11-16-42	11-16-42
			Monthly report.	
LVII+	53	Hach, Curtis and Diehl	11-23-42 to 12-8-42	12-15-42
			Application of rapid mixing apparatus to airplane unit. + These reports were incorrectly labeled LVI-52.	
LVIII	54	Diehl	11-16-42 to 12-15-42	12-16-42
			Monthly report.	
LIX	55	Liggett and Diehl	10-21-42 to 11-14-42	1-15-43
			Study of cobalt compounds derived from mixtures of 2-hydroxy-3-methoxybenzaldehyde with salicylaldehyde and 2-hydroxy-3-ethoxybenzaldehyde.	

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
LX	56	Liggett and Diehl	11-14-42 to 1-1-43	1-15-43
		Attempted preparation of unsymmetrical Schiff's bases.		
LXI	57	Harrison, Brouns and Diehl	10-20-42 to 1-20-43	2-16-43
		Rate Apparatus.		
LXII	58	Brouns and Diehl	12-19-42 to 2-15-43	2-19-43
		Studies on Co-Ox, Co-Ox M, Co-Ox BT, and the mixed compounds Co-Ox BM3, Co-Ox BM10, Co-Ox BM30, Co-Ox BM50, Co-Ox BM70, Co-Ox BM90.		
LXIII	59	Head and Diehl	11-19-42 to 12-29-42	2-5-43
		Allyl rearrangement method for the synthesis of 2-hydroxy-3-ethoxybenzaldehyde; first three steps.		
LXIV	60	Head and Diehl	12-20-42 to 2-27-43	3-4-43
		Completion of studies on allyl rearrangement method of synthesizing 2-hydroxy-3-ethoxybenzaldehyde.		
LXV	61	Diehl	12-15-42 to 2-15-43	2-16-43
		Bimonthly report.		
LXVI	62	Brouns and Diehl	2-15-43 to 3-1-43	3-30-43
		Rate studies on materials containing mixtures of salicylaldehyde and 2-hydroxy-3-ethoxybenzaldehyde, salicylaldehyde and 2-hydroxy-3-methoxybenzaldehyde, and salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde, and 2-hydroxy-3-ethoxybenzaldehyde.		

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
LZVII	63	Liggett and Diehl		
LZVIII	64	Mathews and Diehl	3-6-43 to 3-30-43	4-1-43
LXIX	65	Diehl	2-16-43 to 3-15-43	3-15-43
LXX	66	Liggett, Curtis and Diehl	3-1-43 to 4-10-43	5-5-43
LXXI	67	Liggett, and Diehl	5-20-43 to 8-1-43	
LXXII	68	Diehl	9-1-42 to 4-15-43	4-30-43
LXXIII	69	Hach and Diehl	5-20-42 to 5-20-43	8-11-43
LXXIV	70	Diehl	3-16-43 to 4-15-43	4-19-43

<u>Report Number</u>	<u>Report to NDRC No.</u>	<u>By</u>	<u>Period Covered by Report</u>	<u>Date of Report</u>
LXXV	71	Liggett, Schwandt and Diehl	3-15-43 to 5-30-43	
		Various aldehydes.		
LXXVI	72	Diehl	4-15-43 to 5-14-43	5-17-43
		Monthly Report		
LXXVII	73	Liggett, Curtis, Mathews and Diehl	4-20-43 to 5-5-43	5-27-43
		Co-Ox SS.		
LXXVIII	74	Liggett, Mathews and Diehl	3-1-43 to 6-30-43	
		Solubility of disalicyclethylenediimine in solutions of nitrogenous materials. Vinyl, propionic acid substituents.		
LXXIX	75	Diehl	4-20-43 to 6-30-43	8-13-43
		Fifth and Final Progress Report.		

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AUTHOR(S): Diehl, Harvey

ORIGINATING AGENCY: Iowa State College, Ames, Ia. for Office of Scientific Research *

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June '43	Conf'd	U.S.	Eng.	53	tables, diagr, graphs

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ABSTRACT:

During the period covered by this report, several hundred grams of di(2-hydroxy-3-n-butoxybenzal) ethylenediamine cobalt (Co-Ox SS), a material possessing the highest rate of oxygenation yet observed on any compound, was prepared and shipped to the M.I.T. laboratory for investigation. The search for new compounds was continued, efforts being devoted to the testing of the compounds from numerous aldehydes derived from various commercially available phenols and to substituted acetophenone and propiophenone derivatives. An investigation into the possibility of finding a means of operating the oxygen-producing cycle in solution by dissolving the oxygen-carrying compounds in solutions of nitrogenous materials to produce a compound more closely resembling the hemoglobin of blood, and work on the circulating-solid apparatus were continued until the termination of the contract.

*and Development, NDRC

DISTRIBUTION: Copies of this report obtainable from Air Documents Division; Attn: MCIDXD

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AUTH:

By

George P. Jordan USCO

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