ENCLOSURE (B) 5

RESEARCHES ON ORGANIC STABILIZERS FOR HYDROGEN PEROXIDE

by
CHEM. ENG. LIEUT.
J. ITANI

Research Period: 1944-1945

Prepared for and Reviewed with Author
by U. S. Naval Technical Mission to Japan

December 1945

ENCLOSURE (B)5

LIST OF TABLES AND ILLUSTRATIONS

Table	I(B)5	Effectiveness of H_2O_2 Inhibitors at 90°C	Page 54
Table	II(B)5	Change in H_2O_2 Concentration in Presence of Various Inhibitors	Page 55
Table	III(B)5	Change in H_2O_2 Concentration in Presence of Various Inhibitors	Page 56
Figure	1(B)5	Concentration Drop Curves When Heated at 90°C	Page 57
Figure	2(B)5	Concentration Drop Curves When Placed at Room Temperature	Page 58

ENCLOSURE (B)5

SUMMARY

Organic stabilizers for concentrated hydrogen peroxide solutions have been required ever since the use of hydrogen peroxide for rockets was developed. Inorganic substances are rather unsatisfactory for this application.

In order to discover appropriate stabilizers from the point of view of effectiveness and durability, some preliminary experiments were conducted which show the superiority of quinoline and its derivatives, although no general conclusions have been reached.

I. INTRODUCTION

A. History of Project

As very few investigations have been carried on in Japan on this subject, it was intended to search for the appropriate types of organic compounds by several experiments.

Consequently, it was discovered that aniline, 8-Hydroxy-quinoline, etc., are quite effective, but that they were apt to be oxidized and lose their effectiveness.

Therefore, although superior and more stable substances were desired and searched for in the subsequent experiments, it was in vain and the quinolines remained the best known stabilizers.

One portion of each sample was maintained at 90°C, and its concentration titrated at intervals. Another portion of each sample was maintained at room temperature and titrated in the same manner.

Glycerine is necessary for the production of 8-Hydroxy-quinoline. Since glycerine was difficult to obtain, it was necessary to use its methyl derivatives which were easy to obtain, and are as excellent as the former. These researches were carried on from August, 1944, to the present.

B. Test Procedures

1. A sample containing a definite quantity (0.02gm) of each of several compounds was dissolved in 50cc or concentrated H_2O_2 in a glass bottle which was kept in a water bath at 90°C., and the time to fill a 50cc gas burette with the evolved oxygen gas was measured.

It was assumed that the longer the time to fill it, the more effective the inhibitor was.

2. Equimolecular quantities, equivalent to 0.5 gram 8-hydroxy-quinoline per liter of several organic compounds were added to conc, H_2O_2, heated to 90°C as before, and the concentration of peroxide was titrated with 0.1N potassium permanganate solution at intervals.

Other portions of each of these same samples were kept at room temperature and titrated in the same manner.

C. Experimental Results

No data is available except the concentration drop curves. Table I(B)5 is written from memory and indicates the effectiveness of of various inhibitors as judged by the time required to liberate 50 cc of oxygen at 90°C.

Table II(B)5 shows the change of H_2O_2 concentration with time at 90°C in the presence of various inhibitors. Table III(B)5 shows the results using the same solutions, but maintaining them at an average temperature of 18°C.

The data recorded in Table II(B)5 and III(B)5 is presented in Figures 1(B)5 and 2(B)5 in the form of curves, showing the decrease in the concentration of H_2O_2 with time at 90°C and at room temperature, respectively.

Table I(B)5
EFFECTIVENESS OF H2O2 INHIBITORS AT 90°C*

Excellent	Good	Ineffective
Pyridine	Sodium Pyrophosphate	Salicylic acid
Phosphoric acid	Phenacetine	Tannine
Aniline	a-Naphthylamine	Urea
Diphenylamine	Hippuric acid	Acetanilide
8-Hydroxyquinoline	Hydroquinone	Benzoic acid
		Centralit
		Triphenylamine
		Acetic acid

* Excellent: More than 20 minutes needed.
Good: 10-20 min. needed.
Ineffective or Harmful: less than 10 min. needed.

ENCLOSURE (B)5

Table II(B)5
CHANGE IN H_2O_2 CONCENTRATION IN PRESENCE OF VARIOUS INHIBITORS

H_2O_2 Solution	Inhibitor	Time (hr) 0	5	7	8	10	11	15	16	17	19	20	21	24	25
No. 1	Phenol	75		70			64		15			6			
	Pyrocathechine	75	66			29		2							
	Oxalic acid	75		16								0			
	Phthalic anhydride	75	73			69		30							
	Urea	75			65					34		22			
	Pyridine	75	64			49						4			
No. 2	Blank	75	69			49		5				4			
	Phosphoric acid (0.01 gm/lit)	79	77			74		72							
	Resorcinol	79	75					68				46			
	Aniline	79	70			59		47					30		19
	Quinoline	79	78			77		76				75			73
	8-Hydroxy-quinoline	75	79			77		76						75	
	2-Methyl-Oxy-q	79	79			78		78			76			76	
	2-4-Dimethyl-Oxy-q	79	79			78		78			77				
	Blank	79	76			74		69			61				

Temperature 90°C
Concentration of Inhibitor, 0.0034 moles/lit
Concentrations are given in percent

Table III(B)5

CHANGE IN H_2O_2 CONCENTRATION IN PRESENCE OF VARIOUS INHIBITORS

H_2O_2 Solution	Inhibitor	Days: 0	60	63	64	67	68	69	70	71	72	74	96	103	105	106	112	115	119	120	122	123
No. 1	Pyrocathechine	79										72										68.2
	Oxalic acid	79									74									54.3		
	Phthalic-anhydride	79						76											73.3			
	Urea	79								70.5											46.0	
No. 2	Phosphoric acid (Conc.)	79							71										68.6			
	Resorcinol	79					74									71.6						
	Aniline	79												77.0								
	Quinoline	79	79												78.0							
	8-Hydroxy-quinoline	79															78.3					
	2-M-8-Q	79												78.3								
	2-4-D.M.-8-Q	79											78.3									
	Blank	79			78													76.3				

Temp. Room temp. (March-August 1945), Average temp. 18°C.
Concentration of inhibitor, 0.0034 moles/lit
Concentrations are given in percent.

ENCLOSURE (B)5

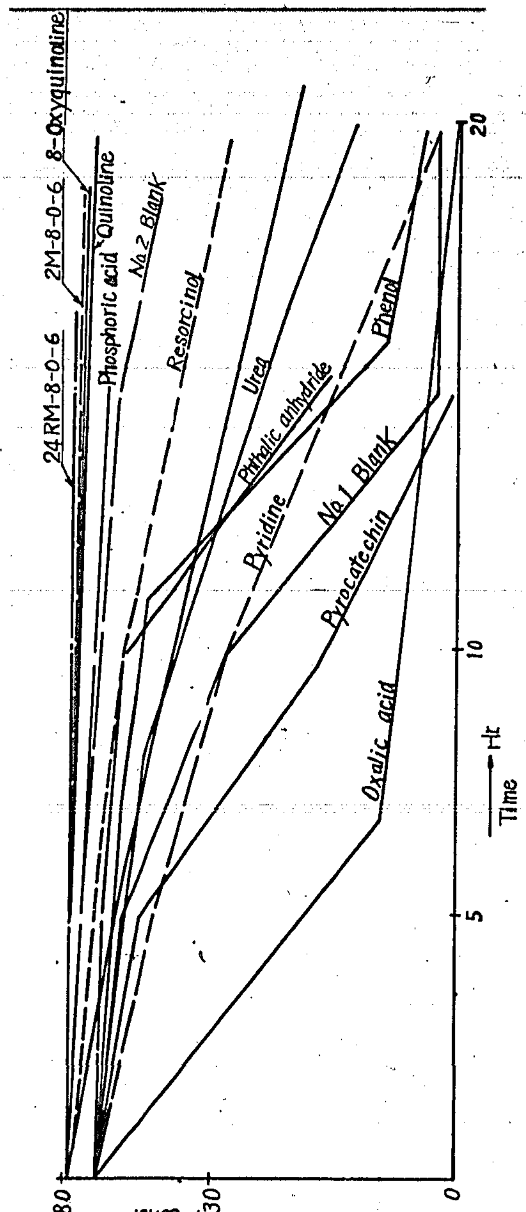

Figure 1 (B)5
CONCENTRATION DROP CURVES WHEN HEATED AT 90°C

ENCLOSURE (B)5

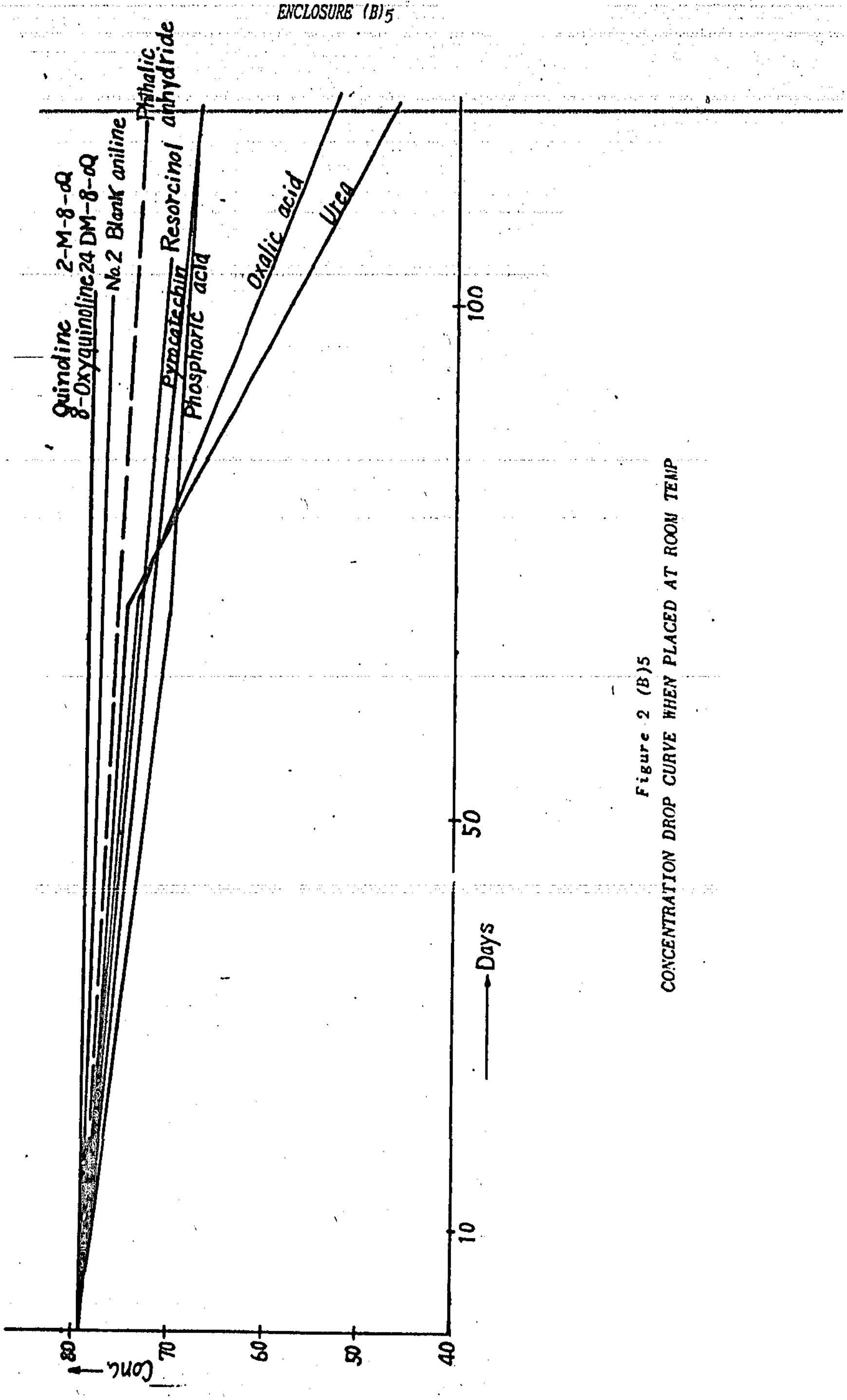

Figure 2 (B)5
CONCENTRATION DROP CURVE WHEN PLACED AT ROOM TEMP