ENCLOSURE (B) 30

R E S E A R C H O N A N T I D E T O N A N T S O F T H E S E L E N I U M S E R I E S

(APPENDIX TO RESEARCH ON THE ANTIDETONANTS OF ANILINE SERIES)

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

To obtain ultra high octane fuel (higher than 100 Octane), the research on the antidetonating compounds of selenium series was attempted. The most desirable agent was diethyl selenide, and, adding it to Stanavo 100 octane fuel (0.8% by volume), 112 Octane rating gasoline was obtained and the horse power was increased about 15%. But it was not used, except perhaps as a take-off fuel, because the availability of Selenium in Japan was meagre.

I. INTRODUCTION

This work was begun in 1937 and finished in 1939. By the use of ultrahigh octane fuel to obtain the maximum horse power with the engines already in service several antiknocking agents were blended in 100 octane fuel. (for example selenium, aniline, or oxo-compounds.) Of these compounds, the selenium series were better than any other compounds because these compounds were effective even in leaded gasoline. The synthesis of several compounds of selenium series were undertaken. When added to leaded gasoline, very high octane fuels were obtained. One of these compounds, diethyl selenide, was blended 0.8% by volume in 100 Octane rating gasoline and tested in a single cylinder and a full scale engine.

II. DETAILED DESCRIPTION

A. Synthesis of Selenium Alkyl Compounds

Five selenium compounds were prepared by the following methods.

1. Dimethyl selenide

Yield obtained was 59% of theoretical in a 3 liter flask. Optimum Conditions: reaction temp. 50-56°, reaction time 2 hrs by following chemical equation:

$$10CH_3KSO_4 + P_2Se_5 + 16NaOH = 5(CH_3)_2Se + 10KNaSO_4 + 2Na_3PO_4 + 8H_2O$$

2. Diethyl selenide

Yield obtained was at max. 87% of theoretical in a lead-lined 50 liter vessel. Flow diagram is shown in Plate I(B)30. Optimum conditions: Reaction temp. 75-80°C, reaction time 6.5 hrs.

$$10C_2H_5NaSO_4 + P_2Se_5 + 16NaOH = 5(C_2H_5)_2Se + 10Na_2SO_4 + 2Na_3PO_4 + 8H_2O$$

3. Diisopropyl selenide

Yield obtained was 48% of theoretical in a 3 liter glass flask. Optimum conditions: reaction temp., 70 - 75°C; reaction time, 3 hrs.

4. Dinormal-propyl selenide

Almost the same as diisopropyl selenide.

5. Diethyl diselenide

It was prepared from the residue of diethyl selenide.

B. Properties of Selenium Alkyl Compounds

Table I(B)30

PROPERTIES OF SELENIUM ALKYL COMPOUNDS

	B.P.(°C)	n_D^{15}	Sp.gr $\frac{15°}{4°}$	Poisonous	odor
Dimethyl Selenide	58.5-59.0°	1.4915	1.4041	No, if in pure state	good
Diethyl Selenide	109.5	1.4833	1.2304		
Dinormal propyl Selenide	154-155	1.4795	1.1481		
Diisopropyl Selenide	150-151	1.4801	1.1570		
Diethyl diselenide	160-188	1.5725	1.6252	Very*	bad

*(4 times as poisnous as tetra ethyl lead)

Purification Method: Diethyl selenide was purified by repeated rectification, usually about 3 times. Length of the rectification tower was about 100cm and filled with active carbon and Raschig rings of glass.

C. Antiknock Properties

Antiknock effect of these Se-compounds in relation to hydrocarbon types was in the following order:

Leaded Case: Aromatics > Olefines > Paraffins > Napththenes
(Best) (Poorest)

Unleaded Case: Paraffins > Aromatics > Naphthenes > Olefines
(Best) (Poorest)

Mean effects of these Se-Compounds were as shown in table II(B)30.

Table II(B)30

MEAN EFFECTS OF Se-COMPOUNDS
(Data shows the increase in octane number)

	Blended Volume				
	0.05mol/L		0.08mol/L		
	Unleaded	Leaded	Unleaded	Leaded	Mean Value
Dimethyl Selenide	6.6	-1.3	9.3	3.5	4.525
Diethyl Selenide	8.1	-0.2	10.8	2.5	5.300
Diisopropyl Selenide	10.3	+3.5	10.6	4.7	7.275
Dinormal-propyl Selenide	7.5	-0.5	8.0	0.5	3.875
Diethyl diselenide	12.2	+4.1	15.8	8.0	10.250

D. Reaction Mechanism of The Decomposition of Diethyl Selenide

Diethyl selenide decomposes at high temperature. It begins to decompose at 250°C and gradually the decomposition becomes more severe. The stages of decomposition are shown by the following chemical formulae:

$$300^\circ-350^\circ \quad (C_2H_5)_2Se = H_2Se + 2C_2H_4^{*}$$

$$400-450^\circ \text{ and then } (C_2H_5)_2Se \longrightarrow 2C_2H_5 + Se$$

$$\longrightarrow Se + C_2H_4 + C_2H_6$$

*350-450°, also occurs-$H_2Se \longrightarrow H_2 + Se$

E. Engine Performance Tests

Engine Performance tests were conducted with these compounds blended with gasoline. Example: Stanavo 100 O.N. aviation gasoline, with 0.8% by vol. Diethyl selenide added, was tested in a single cylinder engine (Kinsei Engine). The results were as shown in Table III(B)30.

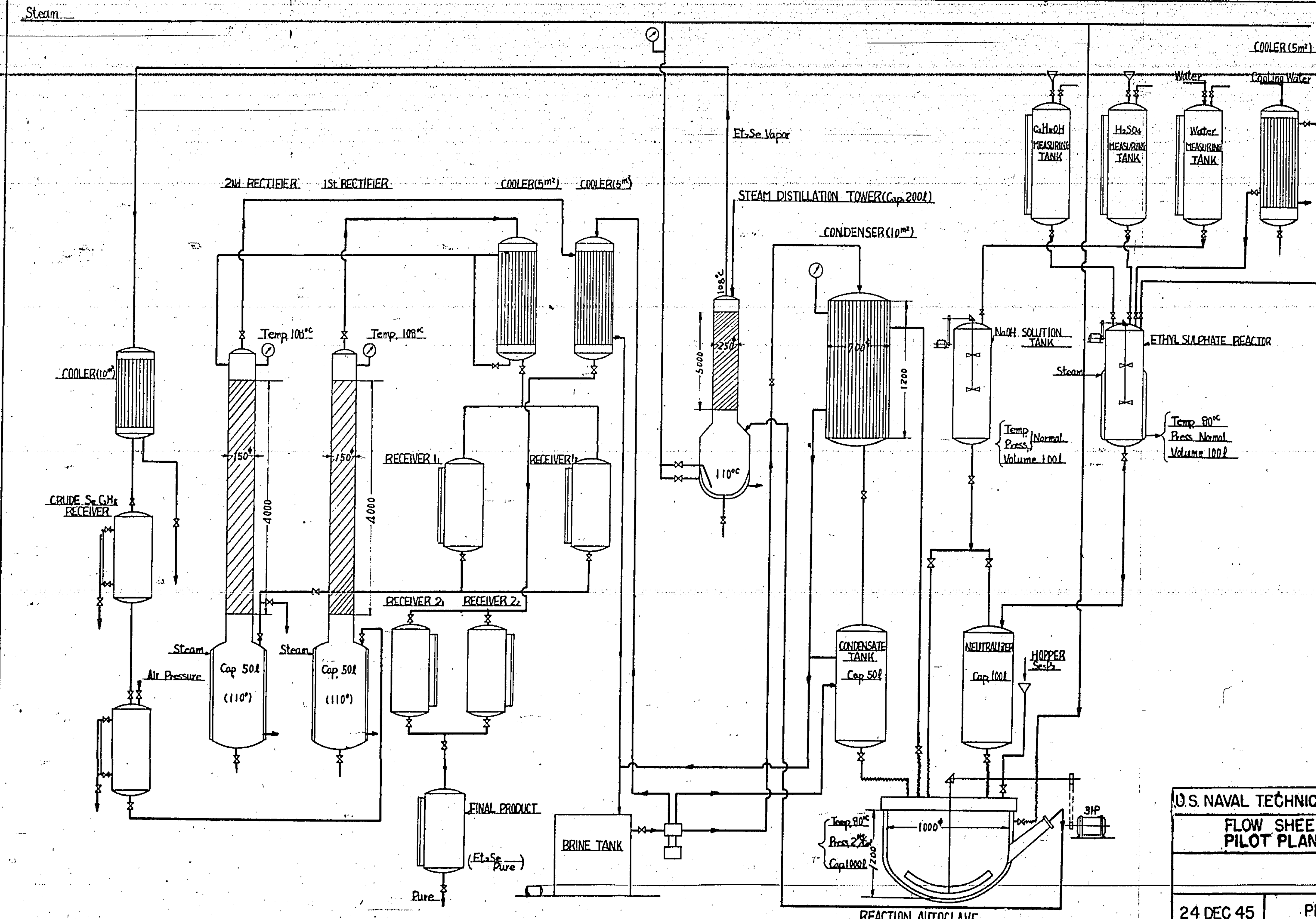
RESULTS OF SINGLE CYLINDER ENGINE TEST

Table III(B)30

	RPM	Boost press. (mm hg)	hp	Fuel Consumption (lit/hr)	Temp. of Exhaust gas (°C)	Temp. of Cylinder wall (°C)
Stanavo Aviation Gasoline. (O.N. 100.8) only	2000	0	44.6	15.89	829	235
	2010	100	33.8	17.60	835	250
	2000	200	58.2	18.70	835	276
	2000	300 (limit)	61.4	19.88	879	289
Same gasoline with 0.8% by vol. $(C_2H_5)_2Se$ added (O.N. 112)	2000	0	45.2	15.51	830	245
	1980	100	52.9	17.12	840	260
	2010	200	59.0	18.70	850	275
	2000	300	65.0	20.68	851	289
	1980	370	67.6	21.95	850	305
	2000	430	72.0	22.50	850	310

III. CONCLUSIONS

The effect of antiknock compounds of the selenium series was additive to Tetraethyl lead and suitable as a blending agent to provide fuel having octane ratings above 100. But the use of this compound was limited to take-off purposes only by the low selenium resources in Japan.



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FLOW SHEET OF DI-ETHYL SELENIDE PILOT PLANT		
24 DEC 45	PLATE I (B) 30	X-38(N)-2