ENCLOSURE (B) 29

RESEARCH ON ANTIDETONANTS OF THE ANILINE SERIES

By

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

To obtain 91 octane rating gasoline from Sumatra crude oil, blending of aniline series antiknock agents was attempted. The most desirable agent was aniline itself, and each one percent of aniline-blended elevated the octane rating from 0.9-2.0. Nine defects of aniline could be avoided by the use of dopes.

I. INTRODUCTION

The octane rating of gasoline produced from Sumatra crude oil cannot reach 91 by adding only 0.15% of tetraethyl lead, the maximum amount of lead for practical use. Attempts were made to obtain 91 octane number aviation gasoline from Sumatra crude oil by the use of some aromatic-amines together with 0.15% of tetraethyl lead. Among all aromatic-amines tested, aniline was the most practical because of the abundance of the resources and the ease of production. Although a gasoline having 91 octane number was obtained by adding one to three percent of aniline and 0.15% of lead from Sumatra crude oil, the aniline-blended gasoline had many faults such as the deposits of residue on the walls of the supercharger and the piston head, the corrosive action on copper and iron, dissolving action on the paint of the oil-tight seams, and the cork float of the carburetor, the swelling action on rubber, and the fact that it was poisonous. Although most of these faults could be prevented by additives, some required the reconstruction of the fuel system of the aircraft. Therefore, the aniline-blended gasoline was not used practically in view of the difficulty of concession of the aircraft engines already in service.

II. DETAILED DESCRIPTION

A. On the Antiknocking Effect;

According to the extensive literature, aromatic-amines, in general, have a remarkable antiknocking effect. Among these aniline is the most practical because it is common. The characteristics of aromatic-amines as antidetonants are as follows.

1. They are effective when added in a concentration of several percent to gasoline.

2. They have an additive effect on gasolines containing tetraethyl lead.

3. They have some defects, among which are low solubility in gasoline and tendency to oxidize.

Many kinds of amines of aromatics and aliphatics were tested and the results are summarized below.

The comparison of the antiknock effect was done by the elevation of the octane number of gasoline to which was added one percent of amines. As shown below methyl aniline, xylidine, mesidine, diphenyl amine and n-methyl p-toluidine are more effective than aniline. However, aniline is the most practical.

Mines	Antiknocking Effect*
Aniline	2.65
p-Toluidine	3.88
1, 3-Xylidine	2.85

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Mines	Antiknocking Effect*
n-Methyl Aniline	3.2
n-Ethyl Aniline	1.6
p-Isopropyl Aniline	2.45
p-Tert. Butyl Aniline	2.20
n-Methyl α-Naphthyl Aniline	1.65
Benzal-p-Toluidine	0.2
Phenyl Hydrazine	-1.6
o-Anisidine	1.14
Phenyl Azide	-3.03
Mesidine	2.85
n-Diethyl Aniline	0.64
Diphenyl Amine	3.9
Methyl Anthranilate	1.15
n-Methyl Formanilide	2.65
n-Nitroso-i-Propyl Aniline	-0.25
2-Methyl Formanilide	-4.0
n-Propyl Amine	0.9
i-Propyl Amine	1.5
Triethyl Amine	0
n-Butyl Amine	0.3
t-Butyl Amine	0.8
Ethyl Amine	0.53
Diethyl Amine	1.30
Triethyl Amine	0.38
Triphenyl Amine	0.23
Diphenyl Ethyl Amine	1.53

*Octane Number Change-CFR (Motor Method)

Therefore, the antiknock effects of aniline on the various base fuels and pure hydrocarbons were measured. Generally, the antidetonant varies its effect with the constituents of the base fuels. (See Tables I(B)29 to IV(B)29.)

The variation of the antiknocking effect of aniline was measured by using several kinds of fuels. (Aniline was blended with the base fuels with 1.5 times by volume of n-butanol.) The properties of the fuels used are shown in Table I(B)29, and the antiknock effects of adding one, two, three, and five percent of aniline are shown in Table II(B)29. It seemed that the effect of aniline on hydrocarbons decreased with the order: normal paraffine, olefine, iso-paraffine and aromatic. Table III(B)29 and IV(B)29 show the increase of octane number of various fuels due to the addition of aniline together with tetraethyl lead.

B. Prevention of Separation of the Aniline Fuels:

The solubility of aniline in ordinary gasoline is about five percent at room temperature, and at low temperatures aniline separates in crystal form which may choke the fuel filter of the engine. The separation of in aniline-blended gasoline is prevented by the use of solvents of which normal butanol is the most effective.

C. Prevention of oxidation of aniline:

The effects of air, sun light, and its own impurities may cause the aniline to change colour. This colour change is due to the presence of aniline black.

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One of the impurities which rapidly accelerates the discoloration of aniline is phenylene-diamine. As the inhibitors of the oxidation of aniline, organic bases, phenol derivatives, ketones, aldehydes, azodyes, and their intermidiates, which have a reducing character, were tested. The results obtained were as follows:

No effect

Enantho-aldehyde	p-Dimethyl aminobenzaldehyde
Dephenyl amine	Dimethyl hydroquinone
Acetone	Tetraline
Pyridine	Diphenyl thiourea

Negative effect (Acceleraters)

o-Nitrobenzaldehyde	α-Naphthylamine
Naphthol	Acetophenone
Diphenylmethane	Calcone

Positive effect

Salicylaldehyde	Quinoline
Paraldehyde	Amylsalicylate
Hydroquinone	

In general, aromatic aldehydes were effective, and benzal aniline was especially excellent in that when 0.1-2% for aniline was added, no discoloration occurred for a long period.

D. Problems in the Practical Use of Aniline:

1. After a performance of long duration in the engine using the three percent of aniline-blended gasoline, considerable black resinous matter was deposited on the parts of the supercharger, inlet pipe, piston ring and piston head.

But when the sludge content was less than 10 mg per 100cc in aniline-blended gasoline, it could be used for more than 50 hrs., especially when benzal aniline was added.

2. Corrosion and deposits of copper metal were both avoided by addition of dipiperidyl or thiourea, 0.1% or 0.01% respectively.

3. Oiltight paints of riveted fuel tank were dissolved especially acryl resin series, but this trouble was also avoided by replacing with acrylnitryl resin type paint.

4. Nitrocellulose paint on the coak float in the carburettor of the engine was also dissolved, but this was prevented by the use of acetyl cellulose paint.

5. Natural rubber was swelled by the aniline-blended gasoline, but synthetic rubber (Buna N) was not.

6. Poisonous effect of aniline vapor. In the aeroplane neither the vapour nor the exhaust gas of the blended gasoline were poisonous and only those engaged in blending aniline with gasoline had to take precautions.

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Inspection for aniline vapour was accomplished by use of the indo-phenol reaction.

III. CONCLUSIONS

A. The most desirable antiknock agent of the aniline series is aniline itself.

B. For every one percent of aniline added, the octane rating of Sumatra gasolines was improved 0.9-2.0 numbers.

C. Several defects of aniline-blended gasoline were avoided, and it was suitable for practical use even in combat planes. However, its solvent action for paints made its storage in riveted tanks on aircraft carriers difficult. Also, the fumes from aniline would be objectionable aboard ship.

Figure 1(B)29

CLOSE UP VIEW OF THE EXPERIMENTAL APPARATUS FOR TETRA-ETHYL-LEAD

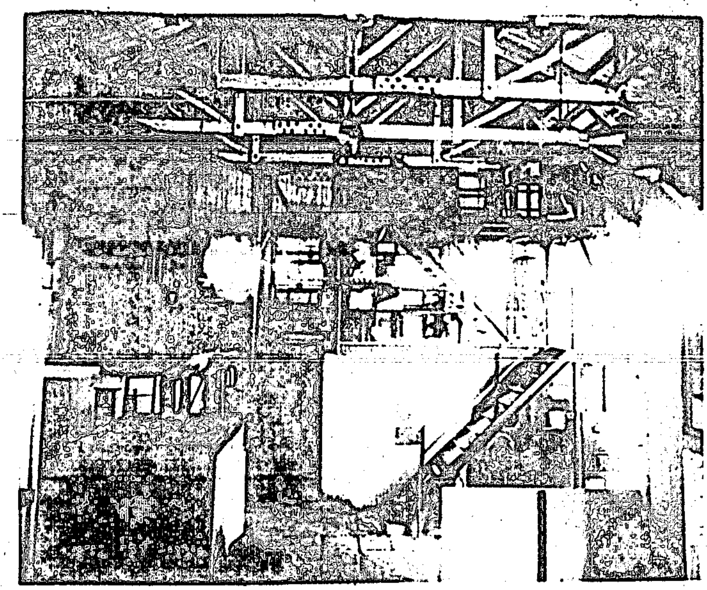

TABLE I(B)29

PROPERTIES OF THE BASE FUELS AND THE SAMPLES USED

		Sub-Standard		Soesoe		Talangimar*	Pendopo*	Mangunjya*	Sanga-Sanga (Borneo)	California	Midway Crude		
		I	II	I*	II						Catalytic Cracking	Thermal Cracking	Hydro-Cracking
Oct. No. (Plain		74.6	61.3	67.1	64.1	66.3	69.6	64.5	71.7	73.8		63.4	60.3
Oct. No. 0.1% Leaded		91	83.8	86.7	85.0	87.1 (0.125 Pb)	89.2	86.4 (0.125 Pb)	91.2	87.2	91	75.8	82.4
Sp. Gr. (15/4)		0.7368		0.7220	0.7402	0.7458	0.7233	0.7448	0.7588	0.7418	0.7448	0.7470	0.7647
Vapour Pressure		0.43	0.36	0.33	0.27	0.48	0.55		0.33			0.32	
Distillation Characteristics	10%	79	76	73	80	67	61	75	80	70	67	78	80
	50%	105	98	95	111	108	91	103	103	106	102	128	154
	90%	134	141	116	139	145	116	141	125	136	126	163	216
	97%	153	169	130	149	159	129		135	152		183	
Constituents of Hydrocarbons	Unsat.	1.2	0.1	0.8	2.0	1.1	0.6	0.5	0.5	0.4	10.3	5.8	1.0
	Arom.	4.7	5.9	10.4	14.1	12.9	13.3	13.7	27.4	9.5	14.3	26.3	9.1
	Napht.	45.2	34.4	30.2	21.7	26.8	36.2	34.3	31.0	40.0	34.3	2.0	26.1
	Paraf.	48.9	59.6	58.6	62.2	59.2	49.9	51.5	41.1	50.1	38.1	65.9	63.8

	Aniline	Butanol	n-Heptane	1-Octane	Methyl Pentane	Toluene
Sp. Gr. (15/4)	1.0250	0.8140	0.6838 (20/4)	0.6918 (20/4)	0.8802	0.8740
B. P. (°C)	118~119/100mm	1115.5~117	98.5	99.9	54~56	105~109
R. I. n_D^{20}	1.5863	1.3972	1.3879	1.3916		

*Sumatra Gasoline

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TABLE II(B)29

EFFECT OF ANILINE ON THE VARIOUS HYDROCARBONS PLUS 0.1% T.E.L.

	Blended Hydrocarbon				
Aniline Added (% Br Vol.)	Octane No. (CFR Motor Method)	30% of n-Heptane	30% of i-Octane	30% of 2-Methyl Pentane	30% of Toluene
0	83.8	79.4	93.5	88.2	92.1
1	85.9	82.6	94.8	90.1	93.3
2	87.8	85.4	95.5	90.6	93.6
3	89.8	86.7	96.0	91.4	93.8
5	92.2	89.7	96.8	92.5	94.0
Mean effect of 1% Aniline	1.95	2.62	0.80	1.71	0.70
	Sub Reference Fuel Only	70%	70%	70%	70%

TABLE III(B)29

EFFECT OF ANILINE ON LEADED SOESOE GASOLINE (SUMATRA)

	% of Lead					
	I			II		
% of Aniline	0.10%	0.15%	0.20%	0.10%	0.15%	0.20%
0	85.0	86.7	87.8	86.7	89.1	90.8
1	86.3	88.9	89.5	88.5	91.1	93.3
2	87.7	89.8	90.6	90.4	92.8	94.5
3	88.5	90.9	91.3	91.4	93.3	95.3
5		92.0				
Mean Effect by 1%	1.27	1.72	1.42	1.85	1.75	1.95

TABLE IV(B)29

MEAN EFFECT PER ONE PERCENT OF ANILINE BY VOLUME ON LEADED GASOLINE

	Base Gas				
	Soesoe				
Leaded (% Br Vol.)	I	II	Talangimar	Pendopo	Mangunjya
0.10%	1.27	1.85	1.40	0.91	2.05
0.15%	1.42	1.95		0.78	1.90

	Base Gas				
			Cracked Gasoline		
Leaded	Sanga-sanga	Cali-fornia	Catalytic	Thermal	Hydrogen-ated Gas
0.10%	0.97	1.00	0.93	2.24	
0.15%	0.88			2.40	1.57