CHAPTER 3

EXPERIMENTAL

3.1 Apparatus and Instruments

Aldrich Kugelrohr Apparatus, model 213-196-2

High Vacuum Pump: Edwards, model E2m2 20035

Infrared Spectrophotometer: Perkin Elmer, model 780

with gravity infrared

spectrophotometer

Fourier-Transform NMR spectrometer: Jeol, model

JNX-FX 90 Q

Mass Spectrometer: Jeol, model JNX-DX 300

3.2 Reagents and Their Purifications

-Hexyl bromide: reagent grade, Fluka, Switzerland

-Magnesium turnings:reagent grade,Fluka,Switzerland

-Stannic chloride anhydrous: reagent grade, Fluka, Switzerland

-Tetrahydrofuran and tolune anhydrous: removed trace of water by refluxing with sodium metal and distilled before use

-Iodine crystals

-Magnesium sulfate anhydrous: reagent grade, Fluka, Switzerland

-Ammonium chloride: satuarated aqueous solution

-Solvent: distilled before use

3.3 Synthesis of tetrahexyltin by Grignard reaction.

n-hexylmagnesium bromide was prepared from magnesium turnings (12.39g, 0.51mole) and n-hexyl bromide (84.19g, 0.51mole) in THF (200ml) contained in 500ml flask fitted with a condensor and drying tube, stirrer, dropping funnel, and dean-stark glass apparatus for trapping the water out from reaction. The reaction had been initiated by adding a small quantities of iodine and the hexyl bromide was added dropwise. When the addition was completed, THF was distilled off from the reaction mixture using dean-stark apparatus. Toluene (200ml) was added and then stannic chloride (22.17g) was added dropwise with continuous stirring. The reaction mixture was refluxed for additional 3 hour. The excess Grignard reagent was decomposed by the addition of small amount of satuarated ammonium chloride solution. The toluene layer was separated and evaporated at diminished pressure to yield the crude product which was distilled at reduced pressure giving tetrahexyltin 35.45g, (91.06% yield based on stannic chloride), b.p. 180-182°C/3mmHg.

Elemental analysis: $C_{24}H_{52}Sn$ requires %C 62.7, %H11.4; found %C 61.34, %H 12.44

IR(neat):$\nu(cm^{-1})$; 2850, 2925, 2960 (aliphaticC-H); see fig 3.1

^{1}H NMR (CDCl$_3$): δ(ppm); 0.713, 0.801, 0.882, 1.266; see fig 3.2

^{13}C NMR (CDCl$_3$):δ(ppm); 9.263, 14.193, 22.861, 27.141, 31.692, 34.346; see fig 3.3

Mass Spectrum: base peak at 375, m-85/e at 373; see fig 3.4

3.4 Determination of antiknock property of the alcohols and tetrahexyltin in gasoline base.

The octane numbers of various gasoline composition bases blended with alcohols and tetrahexyltin were presented in the tables below. The octane determination was made by Petroleum Authority of Thailand (PTT). (ASTM D 2699 and D2700)

Table 3.1   Blend of tetrahexyltin and iso-propyl alcohol with unleaded gasoline base

Blend composition	Unleaded gasoline base (aromatic 45.58% by volume)	
	RON	MON
Base	86.2	81.1
Base + 1g Sn	87.4	81.8
Base + 2g Sn	87.6	82.2
Base + 5%	87.6	82.9
Base + 7%	88.5	84.3
Base + 10%	90.1	85.4
Base + 5% + 1g Sn	88.2	83.0
Base + 7% + 1g Sn	89.2	84.7
Base + 10%+ 1g Sn	91.0	86.1
Base + 5% + 2g Sn	88.4	83.1
Base + 7% + 2g Sn	89.5	85.1
Base + 10%+ 2g Sn	91.3	86.4

The octane number of the blends increased as tin and alcohol content increased. The octane number increased 1-5 units. See fig 3.5.

Table 3.2 Blend of tetrahexyltin and iso-butyl alcohol with unleaded gasoline base

Blend composition	Unleaded gasoline base	
	RON	MON
Base	84.0	80.0
Base + 1g Sn	85.2	79.4
Base + 2g Sn	85.9	79.7
Base + 5%	86.4	80.1
Base + 7%	86.8	81.3
Base + 10%	87.8	82.7
Base + 5% + 1g Sn	87.2	80.5
Base + 7% + 1g Sn	87.4	81.9
Base + 10%+ 1g Sn	88.4	82.9
Base + 5% + 2g Sn	87.4	81.2
Base + 7% + 2g Sn	87.8	82.4
Base + 10%+ 2g Sn	88.8	83.0

The octane number of the blends increased as tin and alcohol content increased. The octane number increased 1-4 units. See fig 3.6.

Table 3.3   Blend of tetrahexyltin, iso-propyl alcohol and
iso-butyl alcohol with unleaded gasoline base
(alcohols were mixed 50:50)

Blend composition	Unleaded gasoline base	
	RON	MON
Base	83.8	80.0
Base + 1g Sn	84.9	80.6
Base + 2g Sn	85.2	81.2
Base + 5%	85.5	81.4
Base + 7%	86.4	82.3
Base + 10%	87.4	82.9
Base + 5% + 1g Sn	86.3	81.8
Base + 7% + 1g Sn	87.4	82.6
Base + 10%+ 1g Sn	88.3	83.4
Base + 5% + 2g Sn	87.0	82.4
Base + 7% + 2g Sn	87.2	82.7
Base + 10%+ 2g Sn	88.8	83.9

The octane number of the blends increased as tin and
alcohol content increased. The octane number increased 1-5 units.
See fig 3.7.

Table 3.4   Blend of tetrahexyltin and iso-butyl alcohol with
             unleaded gasoline base at high octane number
             Light Naphtha 20%   Reformate   80%

Blend composition	Unleaded gasoline base	
	RON	MON
Base	89.5	85.1
Base + 1g Sn	90.0	85.3
Base + 2g Sn	90.4	85.4
Base + 5%	90.3	83.5
Base + 7%	91.7	84.2
Base + 10%	92.1	84.7
Base + 5% + 1g Sn	91.4	83.8
Base + 7% + 1g Sn	91.8	84.5
Base + 10%+ 1g Sn	92.6	84.9
Base + 5% + 2g Sn	91.6	84.0
Base + 7% + 2g Sn	92.0	84.6
Base + 10%+ 2g Sn	93.0	85.1

The octane number of the blends increased as tin and alcohol content increased. The octane number increased 1-3 units. See fig 3.8.

3.5 Determination of octane distribution of the blend of alcohols in gasoline.

This method was distillation and recovered gasoline at 100 °C to determine RON. The octane numbers of gasoline blended with alcohols were presented in table 3.5.

Table 3.5 Octane distribution of the blend of alcohols with unleaded gasoline base

Blend composition	RON
Base + 5% IBA	78.1
Base + 7% IBA	80.1
Base + 10%IBA	82.3
Base + 5% IPA	80.1
Base + 7% IPA	81.3
Base + 10%IPA	86.2
(IBA:IPA, 50:50)	
Base + 5%	78.5
Base + 7%	81.1
Base + 10%	84.4

3.6 Determination of volatility of alcohols in gasoline.
(ASTM D 86 and ASTM D 323)

These tests that were determined by distillation (ASTM D 86) and Reid Vapour Pressure(RVP, ASTM D 323) were presented in table 3.6 and 3.7.

Table 3.6   Distillation of gasoline blended with iso-propyl
alcohol and iso-butyl alcohol

Blend composition	% by volume										
	IBP	10	20	30	40	50	60	70	80	90	EP
Base	40	65	76	88	98	108	116	125	135	145	170
Base+5%IPA	45	61	68	76	88	100	109	118	129	143	170
Base+7%IPA	45	62	70	79	89	99	109	117	127	143	170
Base+10%IPA	45	62	71	80	89	100	109	117	127	143	170
Base+5%IBA	40	60	68	77	88	99	109	117	127	144	170
Base+7%IBA	41	60	68	78	89	99	109	118	127	144	170
Base+10%IBA	45	60	70	78	89	99	109	118	127	145	170
Base+IPA:IBA 50:50											
Base+5%	45	60	68	78	86	97	107	117	127	144	165
Base+7%	45	61	69	78	85	97	107	118	127	145	165
Base+10%	45	61	69	78	85	97	107	118	128	145	165

The distillation was recovery 98-99% by volume.

Table 3.7   Reid Vapour Pressure of gasoline blended with

iso-propyl alcohol and iso-butyl alcohol

Blend composition	RVP (psi)
Base	6
Base + 5% IPA	5.1
Base + 7% IPA	5.4
Base + 10%IPA	5.8
Base + 5% IBA	6.8
Base + 7% IBA	5.5
Base + 10%IBA	5.5
Base + IPA:IBA,50:50	
Base + 5%	5.5
Base + 7%	5.5
Base + 10%	5.8

3.7 <u>Determination of existent gum in gasoline.</u> (ASTM D 381)

The existent gums of gasoline blended with alcohols were

presented in table 3.8 and were calculated by

$$A = 2000(C-D+X-Z)$$

A = existent gum content, mg/100 ml

C = weight recorded for sample and residue, g

D = weight recorded for sample, g

X = weight recorded for blank, g

Z = weight recorded for blank and residue, g

Table 3.8   Existent gums of gasoline blended with iso-propyl

   alcohol and iso-butyl alcohol

Blend composition	Existent gum(mg/100ml)
Base	0.4
Base + 5% IPA	0.4
Base + 7% IPA	0.4
Base + 10%IPA	0.8
Base + 5% IBA	1.0
Base + 7% IBA	0.4
Base + 10%IBA	0.4
Base + IPA:IBA,50:50	
Base + 5%	0.4
Base + 7%	0.4
Base + 10%	0.4

3.8   Determination of Copper corrosion. (ASTM D 130)

Each sample showed a very little corrosion (No.1) at 50°C,

3 hours.

3.9   Determination of Heat of combustion of gasoline blended

   with alcohols.

Heat of combustion of gasoline blended with alcohols were

presented in table 3.9 and were calculated by

$$H = tw - e_1 - e_2 - e_3 / m$$

H = Heat of combustion (cal/g)

w = energy equivalent of calorimeter (cal/°C)

t = net corrected temperature rise (°C)

m = mass of sample (g)

e_1 = correction for heat of formation of nitric acid

= c_1 if 0.0725 N alkali was used for the acid titration

c_1 = militers of standard alkali solution used in acid titration

e_2 = correction in calories for heat of formation of sulfuric acid

= $14(c_2)(m)$ for liquid hydrocarbon fuels

c_2 = percentage of sulfur in sample

e_3 = correction in calories for heat of combustion of fuse wire

= $(2.3)(c_3)$ when using Parr 45c10 nickel-chromium fuse wire

c_3 = centimeters of fuse wire consumed in firing

Table 3.9   Heat of combustion of gasoline blended with

iso-propyl alcohol and iso-butyl alcohol

Blend composition	Heat of combustion(cal/g)
Base	12199.30
Base + 5% IPA	12234.04
Base + 7% IPA	11628.39
Base + 10%IPA	11529.89
Base + 5% IBA	11675.93
Base + 7% IBA	11764.50
Base + 10%IBA	11737.83
Base + IPA:IBA, 50:50	
Base + 5%	12070.25
Base + 7%	12119.91
Base + 10%	11608.01
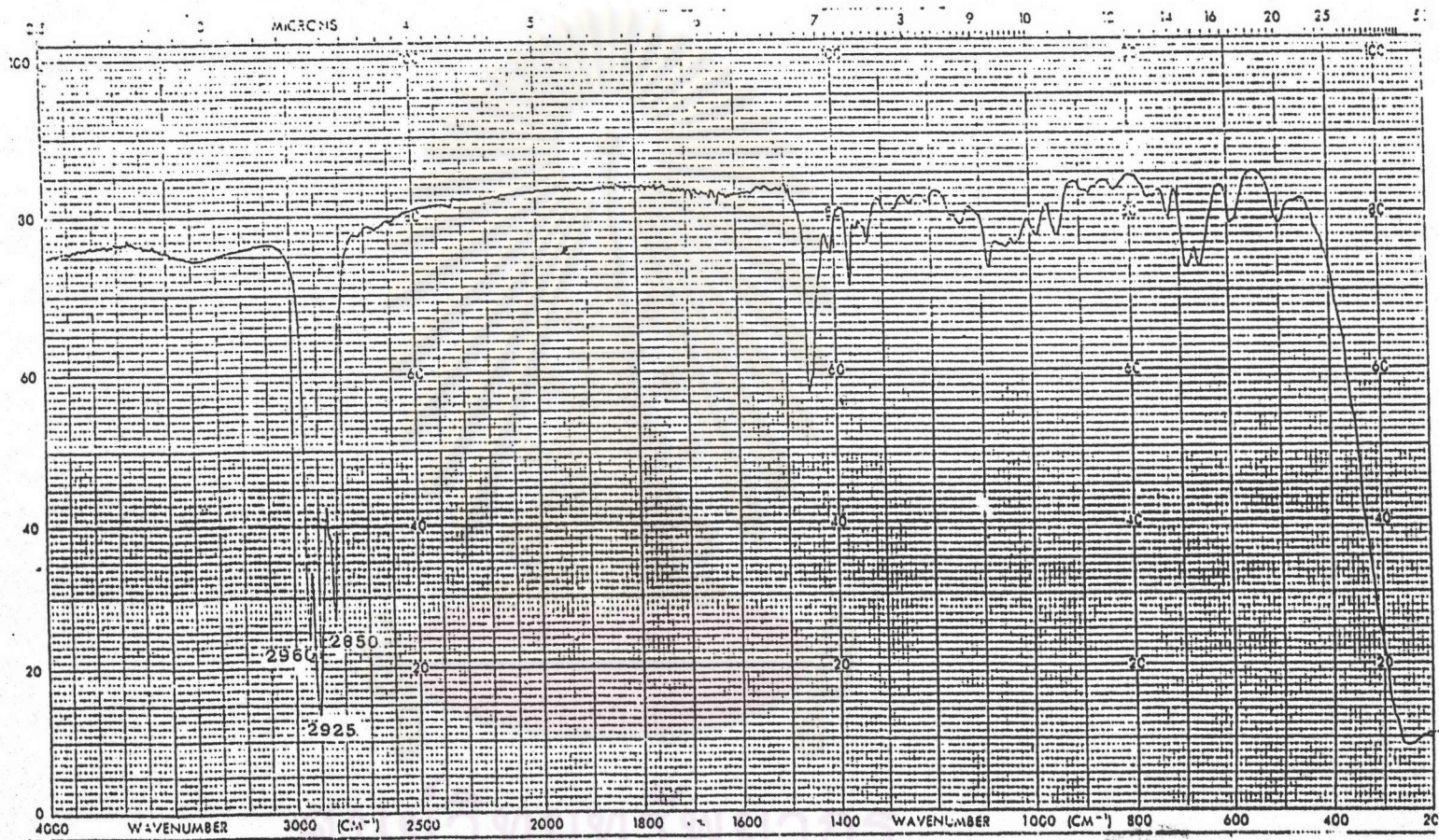
FIG 3.1. IR Spectrum of tetrahexyltin
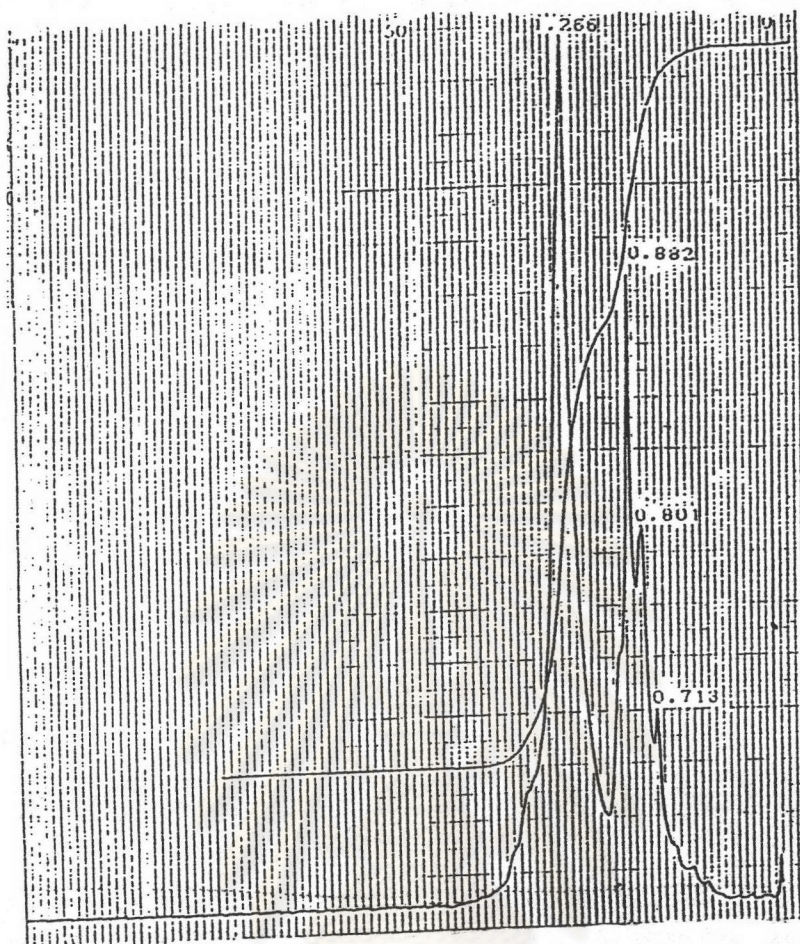
FIG 3.2. ^{1}H NMR Spectra of tetrahexyltin
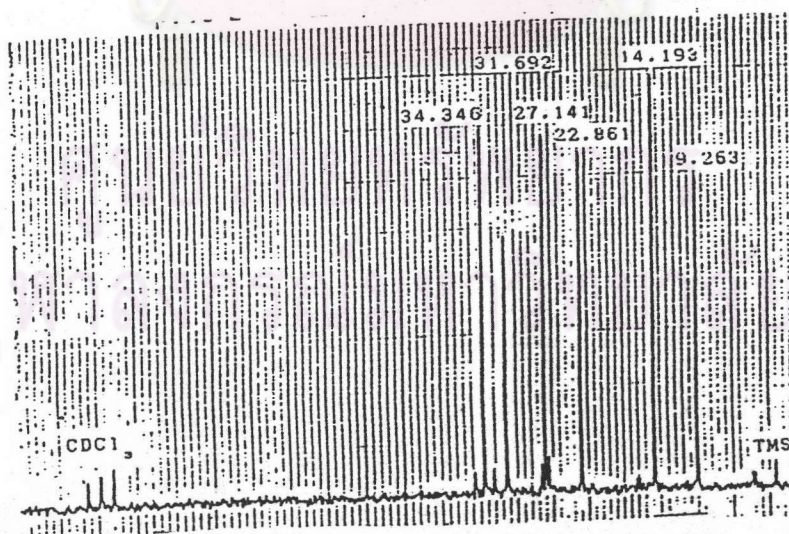
FIG 3.3. ^{13}C NMR Spectra of tetrahexyltin
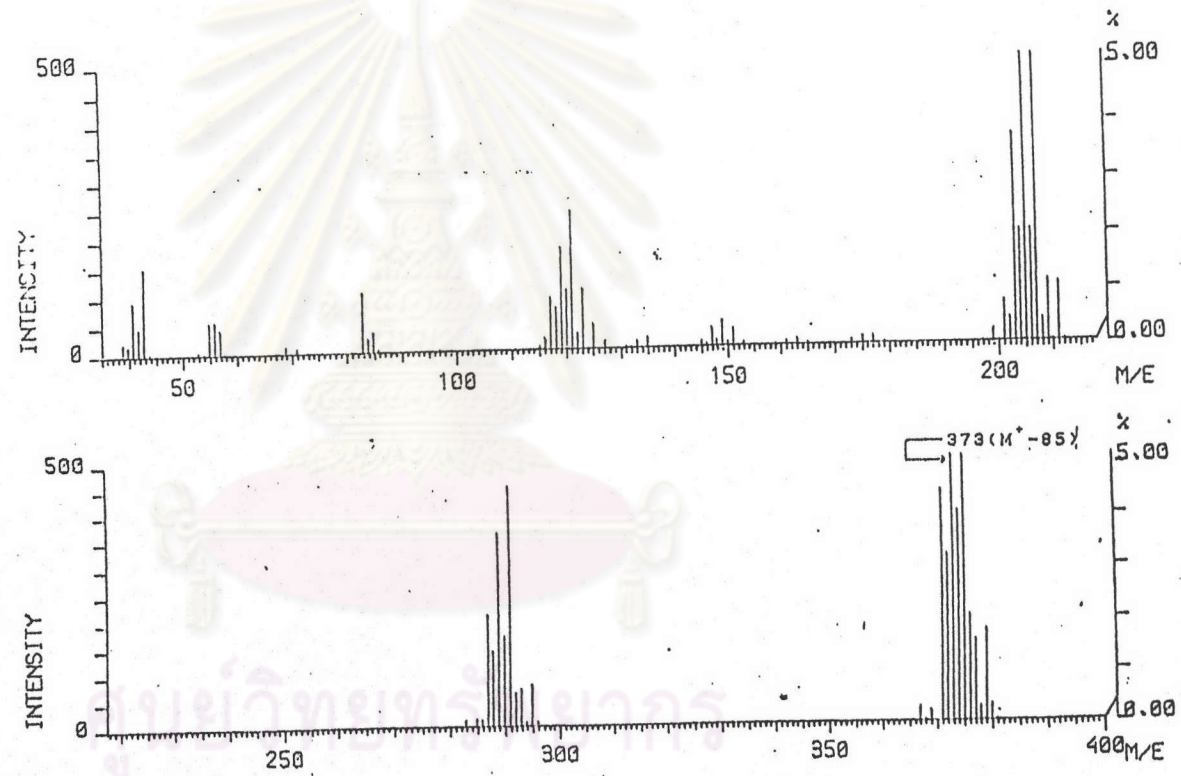
FIG 3.4. Mass Spectrum of tetrahexyltin

FIG 3.5
Effect of IPA on RON

FIG 3.5
Effect of IPA on RON
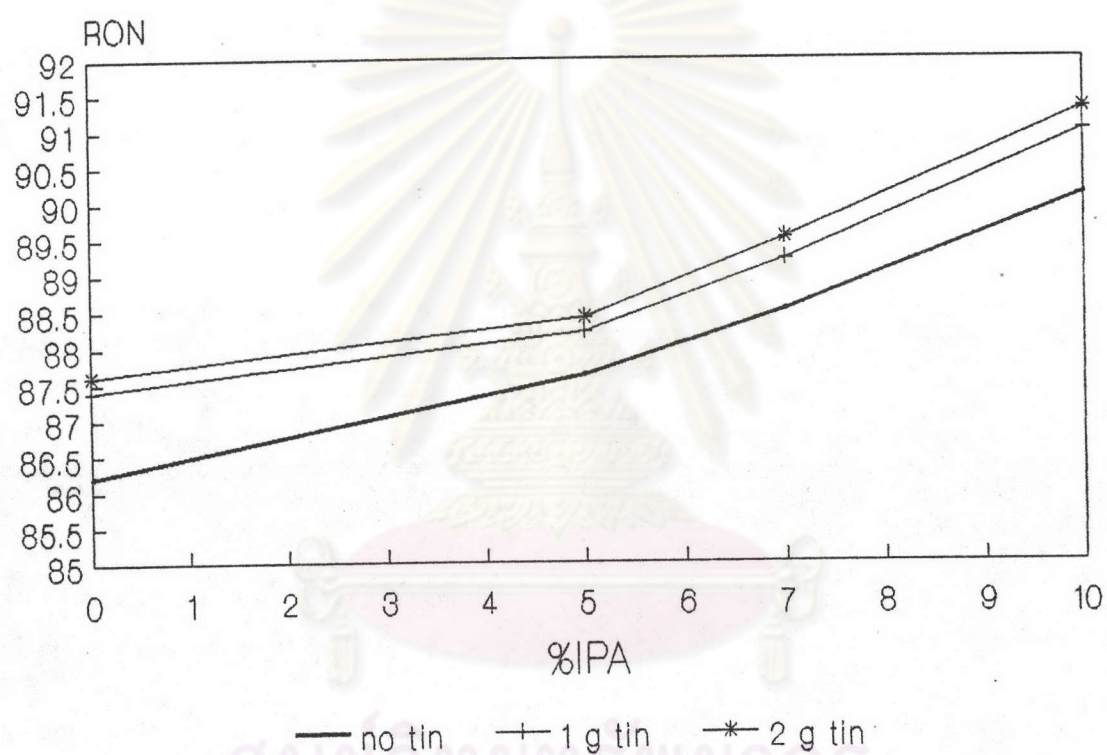
—— no tin   +— 1 g tin   —*— 2 g tin

FIG 3.6
Effect of IBA on RON
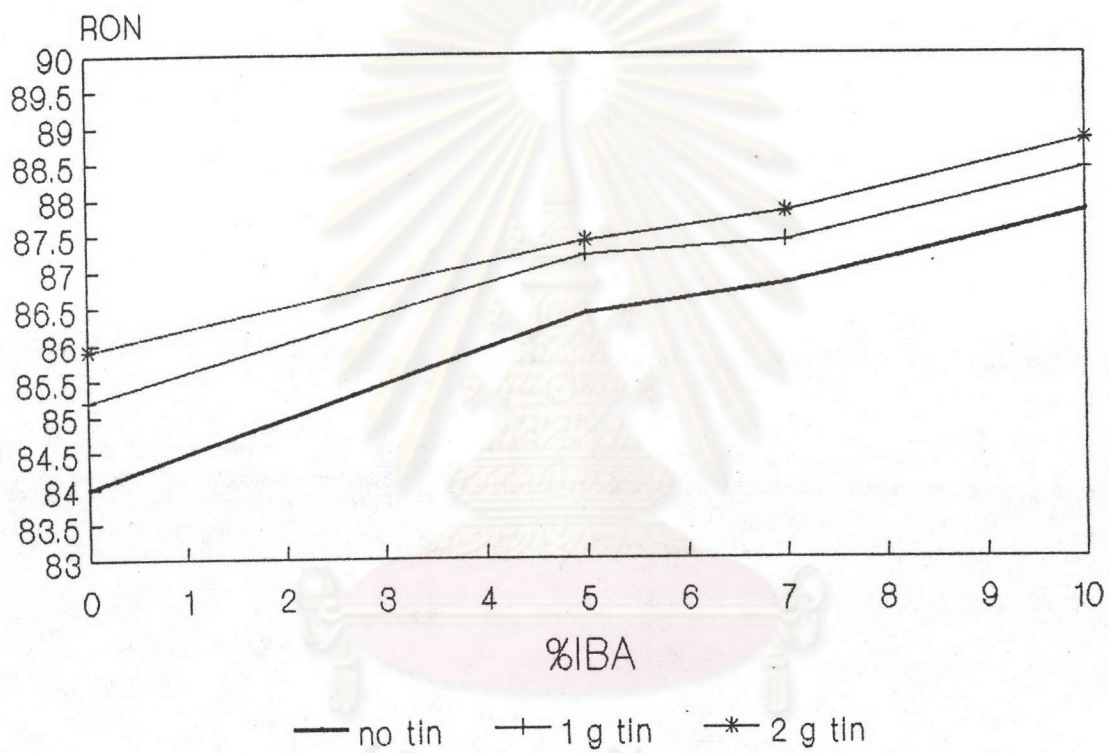
FIG 3.7
Effect of mixed alcohols on RON
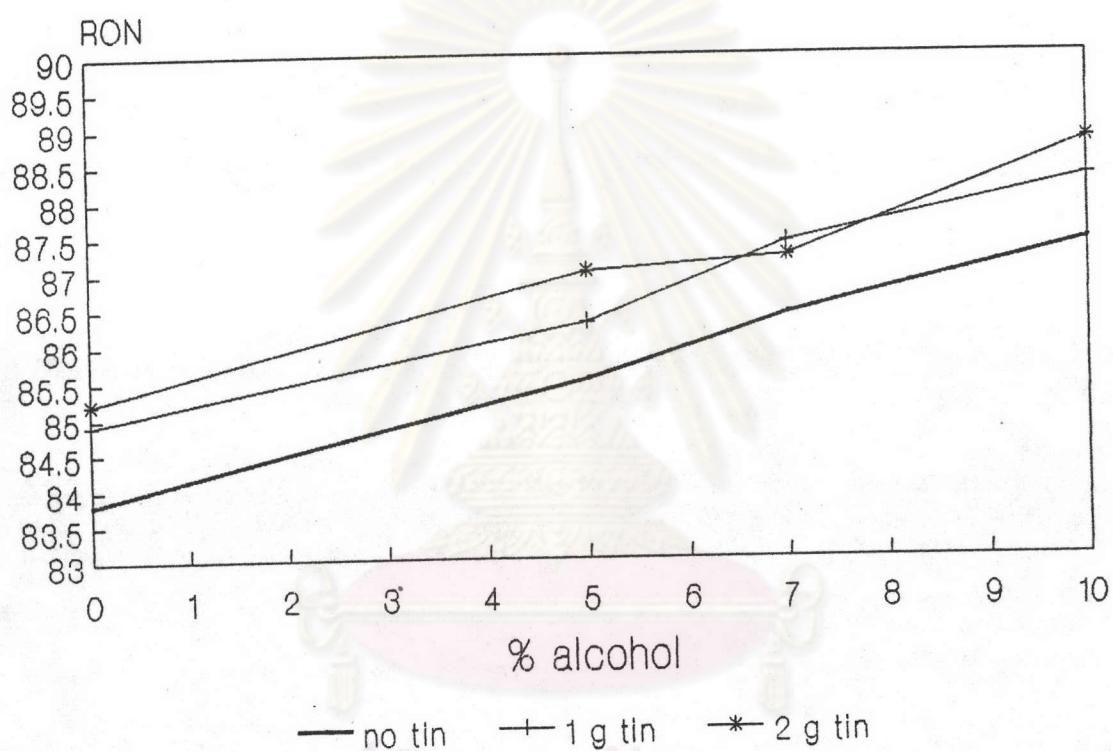
FIG 3.8
Effect of IBA on high RON