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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

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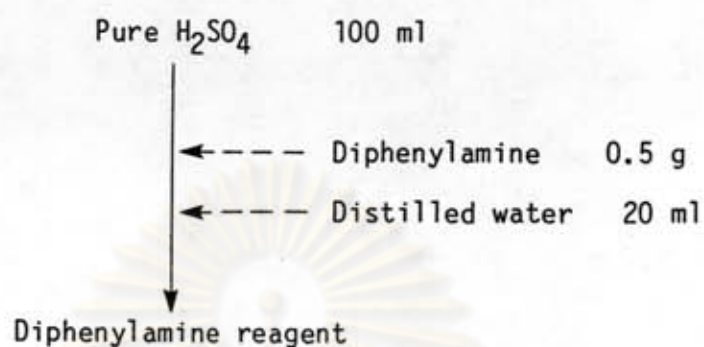
APPENDIXS

Appendix A :   The Preparation of Diphenylamine Reagent.

Pure H_2SO_4 100 ml

← − − −   Diphenylamine   0.5 g

← − − −   Distilled water   20 ml

Diphenylamine reagent

This reagent is used to test the existance of NO_3^- in the test solution.   Fill a few amount of this reagent into the tube and then slowly drop the test solution in the same tube.   If NO_3^- exists in test solution, the layer between these two solutions turns to blue. This reagent can also test the existance of NO_2^- and ClO_3^-.

Appendix B : The Preparation of Copper Nitrate Solution
for the Synthesis of Catalyst.

$Cu(NO_3)_2.3H_2O$ molecular weight = 241.6

CEC of Na-Laponite = 80 meq./100 g-cat.

= 0.8 mmol Na^+/1 g-cat.

= 4.0 mmol Na^+/5 g-cat.

Since 2 Na^+ will be exchanged with Cu^{2+} then for 100% ion exchange,

the needed amount of Cu^{2+} = 2.0 mmol Na^+/5 g-cat.

so, needed amount of $Cu(NO_3)_2.3H_2O$ = $(2.0 \times 10^{-3})(241.6)$

= 0.4832 g

For Cu^{2+} 0.01 N = 0.01 mol Cu^{2+}/ 2000 ml H_2O

For various degrees of ion exchange, various concentrations of
copper nitrate solution are prepared as follows :

Degree of ion exchange(%)	Amount of Cu^{2+} (mol)	Weight of $Cu(NO_3)_2.3H_2O$ (g)	H_2O (ml)
200	4.0×10^{-3}	0.9664	800
150	3.0×10^{-3}	0.7248	600
120	2.4×10^{-3}	0.5798	480
100	2.0×10^{-3}	0.4832	400
75	1.5×10^{-3}	0.3624	300
50	1.0×10^{-3}	0.2416	200

Appendix C : The Analysis Condition of Gas Chromatograph (GC)

A. GC (12)

Analyzing column	:	stainless steel tube 3x4 mm o.d.
		packed with porapac Q 2 m and porapac T 1 m
Reference column	:	stainless steel tube 3x4 mm o.d.
		packed with porapac Q 3 m
Analyzing temperature	:	100 °C
Carrier gas	:	H_2
Carrier gas flow rate	:	40 ml/min
Analyzing products	:	N_2 , CO , CO_2 , H_3COCH_3 , $HCOOCH_3$ and CH_3OH

B. GC (13)

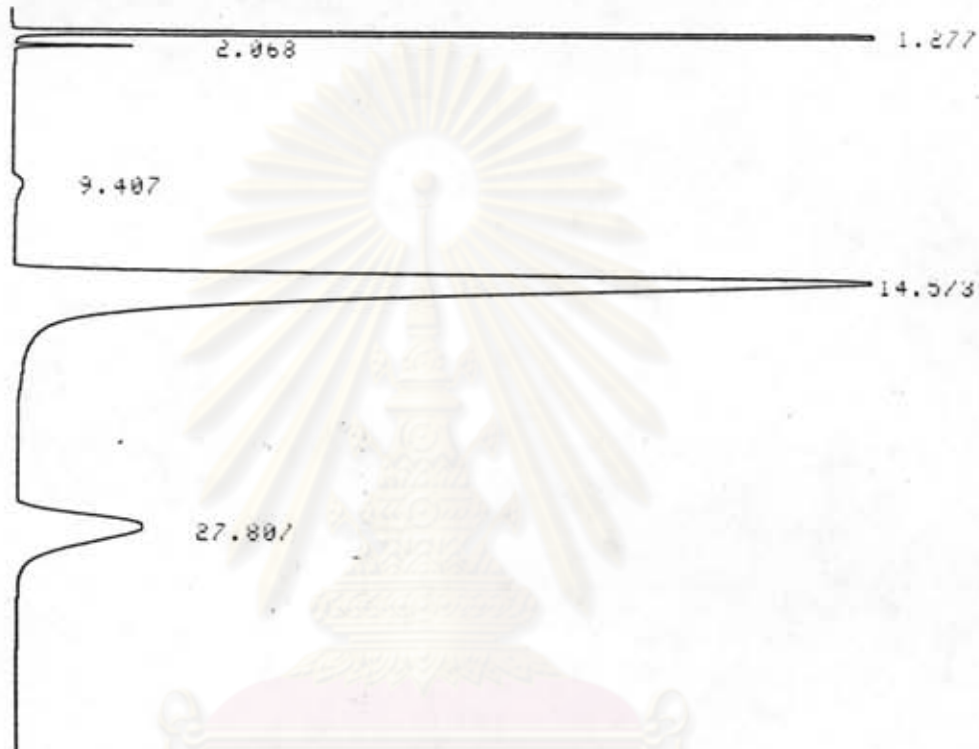|		
Analyzing column	:	stainless steel tube 3x4 mm o.d.
		packed with active carbon
Reference column	:	stainless steel tube 3x4 mm o.d.
		packed with active carbon
Analyzing temperature	:	100 °C
Carrier gas	:	Ar
Carrier gas flow rate	:	40 ml/min
Analyzing products	:	H_2 , N_2 , CO , CO_2 and CH_4

Appendix D : Raw Data from GC , Data Sheet and the Calculation of Catalytic Activity and Selectivity

```
START 1

              2.068                                    1.277

    9.407

                                                     14.573


         27.807




C-R2AX
CHANNEL      1              FILE        0
SAMPLE NO    0              METHOD         41
REPORT NO    369

PKNO    TIME      AREA  MK IDNO    CONC      NAME

  1     1.277    253050            56.8398
  2     2.068      1703             0.3825
  3     9.407      1131             0.254
  4    14.573    159331            35.7887
  5    27.807     29984             6.735
                ---------         ----------
        TOTAL    445199            100
```

DEHYDROGENATION OF METHANOL

DATE ___/___/___   EXPT.NO. _____

CATALYST _____ (NO ____)   WEIGHT OF CATALYST _____ g.

REACTION TEMP. _____ °C   TREATMENT TEMP. _____ °C

W/F _____ g.cat-min/mol   MeOH INPUT(x) _____ mol/min

$Y = 757778.6X + 148.5837$ (y=dial)   DIAL _____

N_2 : MeOH = 5:2   at 273 K N_2 FLOW RATE = _____ mol/min

                        (____°C) = _____ sec/10cc

OUT GAS FLOW RATE _____ sec/10 cc = _____ cc/min at ____°C

                                  = _____ mol/min at 273 K

	PA	% COMPOSITION	FLOW RATE (mol/min) at 273 K
AIR	_____		
H_2	_____	_____	_____
N_2	_____	_____	_____
CO	_____	_____	_____
CH_4	_____	_____	_____
CO_2	_____	_____	_____
		_____	

	PA	MF	PA'	PA'fraction	FLOW RATE
N_2 + CO	_____	_____	N_2 _____	_____	_____
CO_2	_____	_____	_____	_____	_____
H_2O	_____	_____	_____	_____	_____
H_3COCH_3	_____	_____	_____	_____	_____
CH_3OH	_____	_____	_____	_____	_____
$HCOOCH_3$	_____	_____	_____	_____	_____

TOTAL C OUTPUT = _____ mol/min

TOTAL C INPUT = _____ mol/min = CH_3OH INPUT = (TOTAL H_2 INPUT)

TOTAL H_2 OUTPUT = _____ mol/min

$$\text{C BALANCE} = \frac{\text{(total C output)}}{\text{(total C input)}} \times 100 = \underline{\qquad} \times 100 = \underline{\quad} \%$$

$$H_2 \text{ BALANCE} = \frac{\text{(total } H_2 \text{ output)}}{2\text{(total } H_2 \text{ input)}} \times 100 = \underline{\qquad} \times 100 = \underline{\quad} \%$$

C-MOLE BASIS

CH_3OH INPUT = _____ mol/min = TOTAL C OUTPUT

CH_3OH OUTPUT = _____ mol/min

CH_3OH REACTED = _____ mol/min

$$\% \text{ CONVERSION} = \frac{(CH_3OH \text{ reacted})}{(CH_3OH \text{ input})} \times 100 = \underline{\qquad} \times 100 = \underline{\quad} \%$$

$$\% \text{ SEL. } HCOOCH_3 = \frac{2(HCOOCH_3)}{CH_3OH \text{ reacted}} \times 100 = \underline{\qquad} \times 100 = \underline{\quad} \%$$

$$\% \text{ SEL. CO} = \frac{CO}{CH_3OH \text{ reacted}} \times 100 = \underline{\qquad} \times 100 = \underline{\quad} \%$$

$$\% \text{ SEL. } CO_2 = \frac{(CO_2)}{CH_3OH \text{ reacted}} \times 100 = \underline{\qquad} \times 100 = \underline{\quad} \%$$

$$\% \text{ SEL. } H_3COCH_3 = \frac{2(H_3COCH_3)}{CH_3OH \text{ reacted}} \times 100 = \underline{\qquad} \times 100 = \underline{\quad} \%$$

Appendix E : Calculations of Surface Area

1. Calculation of amount of He introduce

$$\frac{(p/760)\ v_m}{273.15 + t} = \frac{(760/760)\ V_{He}}{273.15} \tag{1}$$

$$\bar{V}_{He} = \frac{273.15}{273.15 + t} \cdot \frac{p}{760} \cdot v_m \tag{2}$$

where p = the difference in the level of Hg in manometer (mmHg)

v_m = volume of mercury ball and glass line (ml)

t = room temperature (^oC)

2. Calculation of dead volume

$$\frac{(p/760)(\bar{V}_0 + v_m)}{273.15 + t} = \frac{(760/760)\ \bar{V}_{He}}{273.15} \tag{3}$$

$$\bar{V}_0 = \left[\frac{273.15 + t}{273.15} \cdot \frac{760}{p}\right] \cdot \bar{V}_{He} - v_m \tag{4}$$

3. Calculation of amount of N_2 introduce

$$\bar{V}_{N_2} = \frac{273.15}{273.15 + t} \cdot \frac{p}{760} \cdot v_m \tag{5}$$

4. Calculation of amount of N_2 absorped on catalyst

$$\frac{(p/760)(\bar{V}_0 + v_m)}{273.15 + t} = \frac{(760/760)\,\bar{V}}{273.15} \tag{6}$$

$$\bar{V} = \frac{273.15}{273.15 + t} \cdot \frac{p}{760} \cdot (\bar{V}_0 + v_m) \tag{7}$$

Since $\bar{V}$ is the amount of N_2 free from adsorption

Therefore the amount of N_2 adsorption is calculated from

$$\text{amount of } N_2 \text{ adsorption} = \bar{V}_{N_2} - \bar{V} \tag{8}$$

5. Calculation of specific surface area

5.1 BET equation (multilayer adsorption)

$$\frac{p}{V(p_0 - p)} = \frac{1}{v_n \cdot c} + \frac{(c-1)}{v_n \cdot c} \cdot \frac{p}{p_0} \tag{9}$$

where v_n = amount of N_2 adsorped in multilayer

c = constant

p_0 = vaper pressure of adsorped gas at adsorption temperature (760 mmHg)

p = adsorption equilibrium pressure (the difference of manometer in equation 7)

V = amount of N_2 free from adsorption (equation 7)

Then, the value of $[p/V(p_0 - p)]$ and p/p_0 are calculated and

Calculate the value of slope = $\dfrac{(c-1)}{v_n \cdot c}$ and

$$\text{y-intercept} = \frac{p}{V(p_0 - p)}$$

by using the method of linear regression analysis.

Since, the total surface area $(S) = \dfrac{(t \times 10^{-20}) \cdot v_n \cdot (6.02 \times 10^{23})}{22400}$

$$S = 0.269\ t\ v_n$$

where   t   =   space of one molecular adsorption
at $-195.8\ ^{\circ}C$ t = $16.2\ /\ A^{o2}$
Then S = $4.35\ v_n$
Since $S_{silica\ wool}$ = $6.27\ m^2/g$
Finally, specific surface area of catalyst : S_0 is calculated

$$S_0 = \dfrac{S - 6.27(\text{wt. of silica wool})}{\text{wt. of catalyst}}$$

If the adsorption is in monolayer form, the Langmuir equation is used.

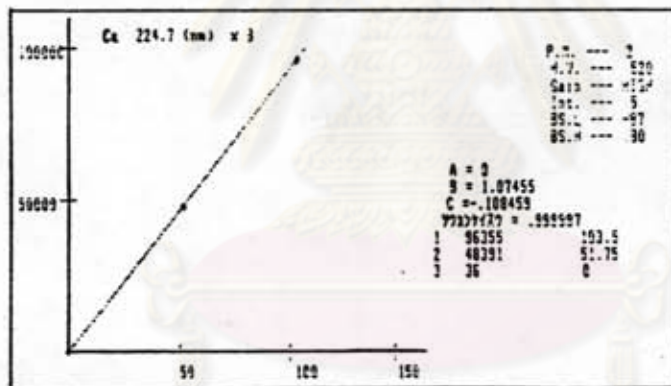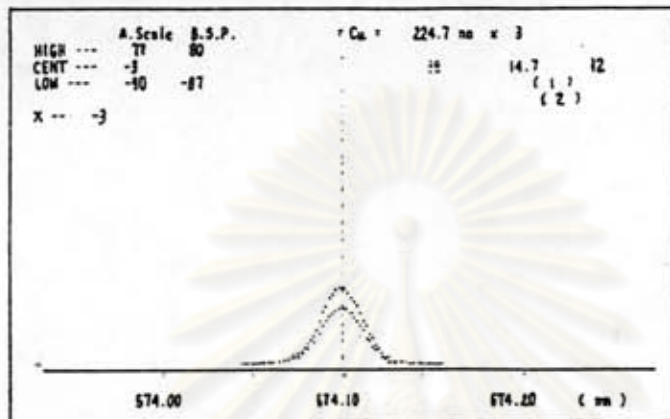5.2 <u>Langmuir equation</u> (monolayer adsorption)

$$\frac{P}{V} = \frac{1}{a.b} + \frac{1}{b} \cdot P$$

where   P   =   adsorption equilibrium pressure (the difference
                     in manometer from equation 7)
        V   =   amount of N_2 free from adsorption
     a, b   =   constant

Appendix F : Data of ICP Measurements

Command (1,2,M,P,K,R,F,C,*) : ?

```
LAPONITE-1      ---    5
                      *** Cu ***        85/11/09   12:19:43
 No.    Lower      Center     Higher      濃度          実濃濃度 (ppm)
 1      136        141        133         6.56287      -.101407
 2      134        140        132         7.04192      -.100893

平  均                                    6.8024       <0
標準偏差                                   0.2395       0.0003
変動係数%                                  3.521        -0.254
試料濃度 =  <0  ppm   試料採取量 = .2015   実濃量 = 100   希釈率 = 496.278
```

```
CU-LAPONITE                          ---    2
                      *** Cu ***        85/11/09   12:12:30
 No.    Lower      Center     Higher      濃度          実濃濃度 (ppm)
 1      783        74344      795         73554.7      78.9297
 2      784        73846      791         73058.3      78.3963

平  均                                    73306.5      78.56
標準偏差                                   248.2        0.2667
変動係数%                                  0.3386       0.3390
試料濃度 =  3.852%   試料採取量 = .2042   実濃量 = 100   希釈率 = 489.716
```

Appendix G : The Calculations of Average Electronegativity

The Sanderson Electronegativity Principle [a)]

Electronegativity is usually defined as the power of an atom to attract electrons independently of the chemical composition of the compound to which the atoms belongs. In a molecule with atoms of difference electronegativity, the electrons will be redistributed such that they will be equally attracted to the nuclei in the bond. This constitutes Sanderson's electronegativity equalization principle. This intermediate electronegativity (S) is postulated to be the geometric mean of the compound atoms of the molecule under consideration. Using the Sanderson electronegativity scale, the partial charge on the atoms of a chemical compound can be calculated as well as its average electronegativity. For a compound $X_x Y_y Z_z$, this intermediate electronegativity is

$$S = (S_X{}^x \ S_Y{}^y \ S_Z{}^z)^{1/(x+y+z)} \qquad (1)$$

Calculations of Average Electronegativity

A. Laponite

The chemical formula of Laponite is $Na_x Mg_{6-x} Li_x (Si_8 O_{20})(OH)_4$

The amount of Na ions in Laponite $= 1.1639$ mmol/g-cat. [b)]
$= 0.0268$ g/g-cat.

equal to

$$\frac{xNa}{xNa + (6-x)Mg + xLi + 8Si + 20(O) + 4(OH)} = 0.0268$$

substitution with molecular weight : Na = 23 , Al = 27, Mg = 24, Si = 28 , O = 16 , OH = 17 and Li = 7

Thus,   x   =   0.8871

then, the chemical formula of Laponite is

$$Na_{0.8871}Mg_{5.1137}Li_{0.8871}(Si_8O_{20})(OH)_4$$
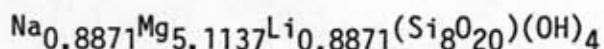
Substitution this formula with electronegativity of each element :
  H^+ = 2.1, Al = 1.5, Mg = 1.2 , Si = 1.8 , O = 3.5 and Li = 1.0

Then, calculation of average electronegativity of Laponite using (1)

$$\underline{S \ = \ 2.50}$$

B. Montmorillonite

The chemical formula of Montmorillonite is $Na_xAl_{4-x}Mg_x(Si_8O_{20})(OH)_4$

The amount of Na ions in Montmorillonite   =   1.4538   mmol/g-cat.[b]
                                             =   0.0334   g/g-cat.

equal to

$$\frac{xNa}{xNa + (4-x)Al + xMg + 8Si + 20(O) + 4(OH)} = 0.0334$$

substitution with molecular weight

Thus,   x   =   1.0768

then, the chemical formular of Montmorillonite is

$$Na_{1.0768}Al_{2.9232}Mg_{1.0768}(Si_8O_{20})(OH)_4$$
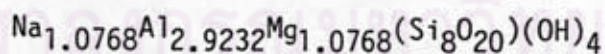
Substitution this formula with electronegativity of each element
Then, calculation of average electronegativity of Montmorillonite by
using (1)
Then, $\underline{S \ = \ 2.64}$

a) Catalytic Reviews : Science and Engineering, Vol.24, No.3, 1982:418
b) Data from ICP measurements.

Appendix H : Data of Thermal Gravimetric (TG) Analysis

Table 4-8 Amount of H_2O desorped from various degrees of ion exchanged of Cu-Lapo at treatment temperature of 800°C

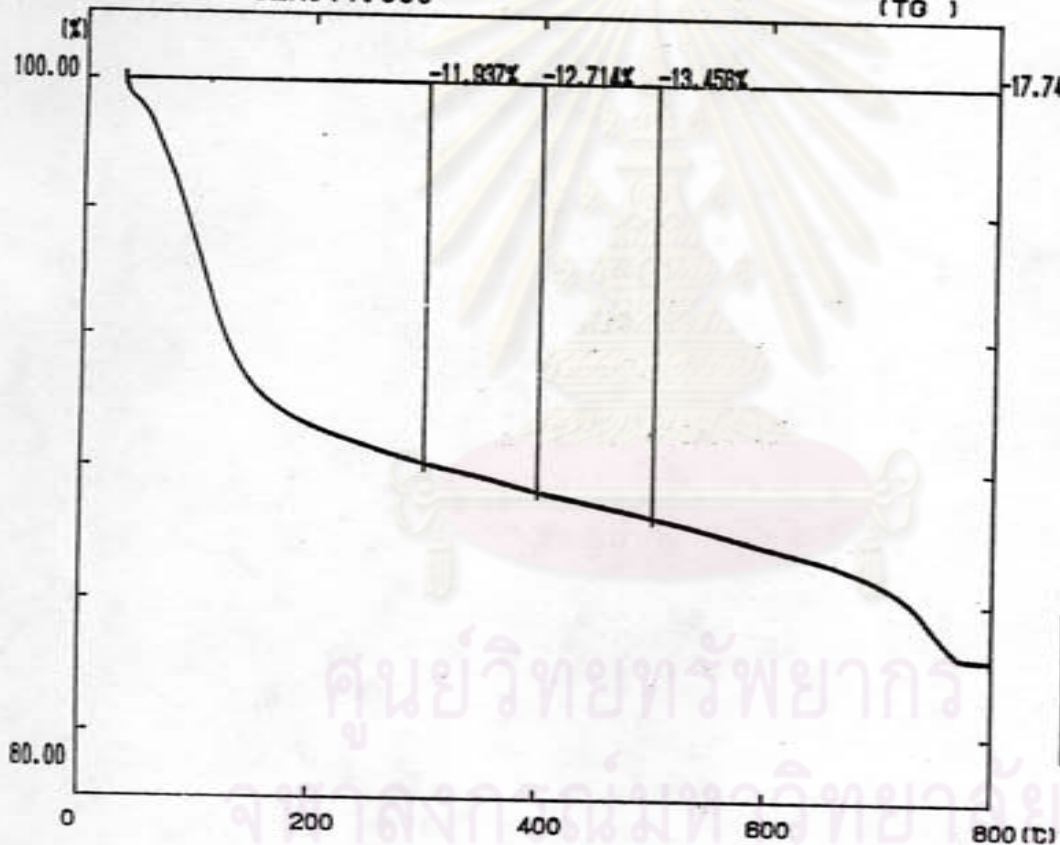| Catalyst	Amount of H_2O desorped (g/g-cat.)
Cu-Lapo 200	0.1577
Cu-Lapo 150	0.1446
Cu-Lapo 120	0.1498
Cu-Lapo 100	0.1774
Cu-Lapo 50	0.1426
Na-Laponite	0.1543

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

THERMAL ANALYSIS DATA

FILE NAME   SEX011.000   (TG)

DATE 89/12/01

MEASURING CONDITIONS
SAMPLE NAME   Cu/Iapo100
SAMPLE SIZE   41.200mg
SAMPLING INT   1.0sec
ACQUIS DATE   89/12/01

HEATING PROGRAM
        RATE   TEMP   TIME
  1   10   800   0

COMMENT

MEMO

SHIMADZU CORP.

APPENDIX I : The details of calculation for amount of Na^+ and Cu^{2+} ions base on dry catalyst.

Catalyst	Amount of H_2O[a] desorption (g/g-cat.)	Amount of ions[b]		Amount of ions[c]	
		Cu^{2+}	Na^+	Cu^{2+}	Na^+
		(mmol/g-cat.)		(mmol/g-cat.)	
Cu-Lapo 200	0.1577	0.5921	0.0694	0.7030	0.0824
Cu-Lapo 150	0.1446	0.5188	0.0908	0.6065	0.1062
Cu-Lapo 120	0.1498	0.4563	0.1180	0.5367	0.1388
Cu-Lapo 100	0.1774	0.2907	0.2098	0.3534	0.2551
Cu-Lapo 50	0.1426	0.1984	0.4008	0.2314	0.4675
Na-Laponite	0.1543	-	0.9846	-	1.1643

a) data from TG measurements

b) data from ICP measurements

c) calculation base on dry catalyst.

VITA

Miss Chatsuda Pantawong was born on December 20, 1964 in Bangkok, Thailand. In 1986, she received the Bachelor Degree of Science, major in Chemical Engineering from the Faculty of Science, Chulalongkorn University. After graduation, she continued her study for Master Degree in the field of Petrochemical Technology at The College of Petroleum and Petrochemistry, Chulalongkorn University. In 1987, she was one of the representatives from Thailand participated in The Ship for Southeast Asian Youth Program for about 2 months. Since September 1988, during her study for Master Degree, she got the scholarship from Waseda University, Japan as a research student there for 2 years. By the end of this year, after her graduation, she will get the industrial training in Japan for a period of time and in the near future she will go back to work in the Petrochemical Industry in Thailand.

March, 1990.