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LOW-COST SOLAR ARRAY PROJECT. TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of SiCl_4 "

Fourth Quarterly Report

By
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April 15, 1980

Work Performed Under Contract No. NAS-7-100-955382

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Solar Energy

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LOW-COST SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of SiCl_4 "

FOURTH QUARTERLY REPORT

April 15, 1980

CONTRACT NO. 955382

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The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

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LOW-COST SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of SiCl_4 "

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Department of Chemistry
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ABSTRACT

Reaction kinetic measurements on the hydrochlorination of SiCl_4 and m.g. silicon metal were last reported as a function of reaction temperature, reactor pressure and H_2/SiCl_4 feed ratio.

The same reaction has been studied in the presence of a copper catalyst. The presence of copper approximately doubles the reaction rates.

A cement-type copper supplied by Union Carbide was evaluated at 5 wt% loading. After an induction period of about 22 hours, it began to show significant catalytic activity. Reaction kinetic measurements were then made as a function of reaction temperature (450°, 500°C), reactor pressure (300, 500 psig) and H_2/SiCl_4 feed ratio (1.0 and 2.8). Another copper compound (CuCl) also was evaluated as a catalyst at 5 wt%. With CuCl , there was no induction period and full catalytic activity was observed soon after the reactor was brought to reaction conditions. Both cement copper and CuCl show about the same catalytic activity by doubling the reaction rate. Results of the copper studies provide some experimental evidence on the mechanism of the hydrochlorination reaction and on the nature of the copper catalyst.

INTRODUCTION

Work on the JPL Government Contract No. 955 382 began in April 1979 to study the hydrochlorination of SiCl_4 and m.g. silicon metal to SiHCl_3 . This report is the fourth Quarterly Report in the series. Reaction kinetic measurements as a function of reaction temperature, reactor pressure and H_2/SiCl_4 feed ratio were last reported. Activities during this quarter included reaction kinetic measurements in the presence of a copper catalyst. A cement-type copper supplied by Union Carbide and cuprous chloride were studied as catalysts for the hydrochlorination reaction. Results are discussed in the following.

DISCUSSION

The laboratory scale stainless steel reactor for the hydrochlorination of SiCl_4 and m.g. silicon metal to SiHCl_3 is schematically shown in Figure I. The design and function of the hydrochlorination apparatus were reported in detail in the first Quarterly Report (DOE/JPL 955 382-79/1). After some reaction kinetic measurements, the same experiments on the hydrochlorination reaction were repeated with copper added as catalyst. The catalytic activity of copper is measured by comparison with the reaction kinetic data obtained with and without copper added.

A. Reaction Kinetic Measurements with 5% Cement Copper

A series of experiments was carried out to study the hydrochlorination of SiCl_4 and m.g. silicon metal to SiHCl_3 in the presence of 5 wt% cement copper (based on Si charged). This cement-type copper, supplied by Union Carbide, is a mixture of CuO , Cu_2O and Cu^0 . A mixture of 180 g 65 x 150 mesh silicon metal and 9 g

cement copper powder (average 10 microns) was thoroughly mixed and carefully charged into the reactor tube. The reactor was sealed and pressurized with hydrogen gas. It was brought up to reaction conditions in the usual manner. An induction period of about 22 hours was noted, during which no catalytic activity was observed. Then, the added copper began to show significant catalytic activity. The activity of the Si mass bed with 5% cement copper as a function of reaction time is shown graphically in Figure II. In Figure II, the % SiHCl_3 conversion is plotted against the % Si conversion in the mass bed. The % Si conversion is defined as the weight of Si consumed divided by the weight of the initial Si charged. It is directly related to the reaction time to reflect the "age" of the mass bed. At the start of the experiment (0% Si conversion), the presence of cement copper actually shows a somewhat slower reaction rate than that obtained under similar reaction conditions with no copper added (dotted line in Figure II). After 22 hours of reaction, the presence of copper began to show some catalytic activity. After about 25% Si conversion, the reactivity of the Cu/Si mass bed stabilized. The nature of this induction period is discussed later in Section D on the reaction mechanism.

A series of experiments was then carried out to measure the rate of the hydrochlorination reaction as a function of reaction temperature (450°, 500°C), reactor pressure (300, 500 psig) and H_2/SiCl_4 feed ratio (1.0 and 2.8). Table I summarizes the experimental data obtained from the hydrochlorination reaction in the presence of 5 wt% cement copper at 500 psig, 500° C and H_2/SiCl_4

ratio of 2.8. Data in Table I are also presented in Figure III by plotting the % SiHCl_3 conversion and the % SiH_2Cl_2 conversion versus residence time. Also plotted in the same graph are experimental data previously obtained from the same hydrochlorination reaction under similar conditions but with no copper added. The graphs in Figure III show that the presence of copper significantly increases the reaction rate. The number in parentheses in Figure III indicates the % Si conversion at which the kinetic measurements were made. When the same experiment was repeated at a lower reaction temperature of 450°C , the presence of copper shows a more pronounced effect on the reaction rate. Results of this experiment are summarized in Table II. The same data are plotted in Figure IV together with previously obtained results from the same reaction with no copper added. The reaction rate in the presence of copper is approximately doubled in comparison with that obtained without copper. For example, in the presence of copper, 23% conversion to SiHCl_3 is observed at 30 seconds residence time (solid line, Figure IV). With no copper added, the same 23% SiHCl_3 conversion is achievable at a residence time twice as long (60 seconds, dotted line in Figure IV). The effect of copper on the reaction rate was studied at a lower reactor pressure of 300 psig. Table III and Table IV summarize the results of the hydrochlorination reaction rate studies in the presence of 5% cement copper at 300 psig and 500°C but at different H_2/SiCl_4 feed ratios of 1.0 and 2.8, respectively. The same data in Table III and Table IV are plotted in Figure V and in Figure VI, respectively, together with previous experimental results obtained from the same reaction with no copper

added. Results of these experiments at 300 psig are similar to those obtained at 500 psig. In the presence of copper, the rate of the hydrochlorination of SiCl_4 and m.g. silicon metal to SiHCl_3 increases by approximately 100% in comparison with those obtained under the same reaction conditions but with no copper added.

B. Reaction Kinetic Measurements with 5% CuCl

Another copper compound is evaluated as catalyst for the hydrochlorination of SiCl_4 and m.g. silicon metal to SiHCl_3 . Cuprous chloride, CuCl , is known to react with Si metal⁽¹⁾ in a displacement reaction,

The copper atoms generated from the reduction of CuCl with Si can diffuse into the silicon crystal lattice. This "plating" action deposits copper onto the silicon particle surface to form what is generally known as Cu-Si alloys. This reaction occurs at temperatures of about 300°C. Under the reaction conditions of 400°C to 550°C for the hydrochlorination reactions, this Cu-Si alloy formation would undoubtedly occur very rapidly.

A series of experiments in the presence of 5 wt% CuCl was carried out in the same manner as those with cement copper. A sample of cuprous chloride was ground and sieved through a 400 mesh sieve (sieve opening, 38 microns). A mixture of 180 g 65 x 150 mesh (210 x 105 microns) m.g. silicon metal and 9 g of this CuCl powder was thoroughly mixed and carefully charged into the hydrochlorination reactor. The reactor was sealed and pressurized with hydrogen gas. It was brought up to reaction conditions in the

usual manner. In contrast to the case with cement copper, there was not induction period observed with CuCl . Full catalytic activity was observed soon after the hydrochlorination reaction was brought up to experimental conditions. The absence of an induction period is clearly shown in Figure VII. The reaction kinetic data in Figure VII show that the reaction rate at the start of the experiment (0% Si conversion) is about the same as those obtained after about 25% of the Si metal has been consumed in the mass bed. Reaction kinetic measurements were carried out as a function of reaction temperature (400° , 450° and 500°C), reactor pressure (300, 500 psig) and H_2/SiCl_4 feed ratio (1.0 and 2.8). Table V summarized the experimental results obtained from the hydrochlorination reaction in the presence of 5% CuCl at 500 psig, 500°C and H_2/SiCl_4 feed ratio of 2.8. Data in Table V are presented in Figure VIII by plotting the SiHCl_3 conversion and the SiH_2Cl_2 conversion versus residence time. Also plotted in the same graph are experimental data previously obtained from the same hydrochlorination reaction under similar conditions but with no copper added. The graphs in Figure VIII show that the presence of 5% CuCl approximately doubles the reaction rate in comparison with that with no copper added. For example, in the presence of copper, 31% SiHCl_3 conversion is obtained at 30 seconds residence time. Without copper, about 65 seconds residence time is required to produce the same 31% SiHCl_3 conversion. Similarly, Table VI and Figure IX summarize the reaction kinetic data obtained under the same conditions but at a lower reaction temperature of 450°C . At lower reaction temperatures, the presence of copper appears to show a

more pronounced effect (see Figure IX). For example, in the presence of 5% CuCl, 28% SiHCl₃ conversion is obtained at 40 seconds residence time. On the other hand, 108 seconds residence time is required to achieve the same 28% SiHCl₃ conversion with no copper. The presence of copper has increased the rate of the hydrochlorination of SiCl₄ and m.g. silicon metal to SiHCl₃ by a factor of about 2.7. The same experiments were repeated at a lower reactor pressure of 300 psig. Table VII and Table VIII summarize the experimental data obtained at 300 psig and a H₂/SiCl₄ feed ratio of 1.0 but at different reaction temperatures of 500°C and 400°C, respectively. Data in Table VII and Table VIII are also plotted in Figure X and Figure XI, respectively, together with previously obtained experimental data obtained under similar conditions but with no copper added. The reaction kinetic data obtained at 300 psig is similar to those obtained at 500 psig. Interestingly, Figure XI shows that at a reactor temperature as low as 400°C, a respectable 24% conversion to SiHCl₃ is achievable at 180 seconds residence time in the presence of copper.

The performance of cement copper and CuCl in the hydrochlorination reaction is shown in Figure XII. In Figure XII, the reaction rate data obtained from the cement copper and CuCl experiments are plotted in the same graph together with the experimental results obtained under similar conditions but with no copper added. The numbers in the parentheses in Figure XII give the % Si conversion which is a direct measurement on the "age" of the Si mass bed. Data in Figure XII shows that, when properly activated through an induction period, cement copper gives about the same catalytic

activity as those obtained with CuCl in the hydrochlorination reaction. However, from a process point of view, cuprous chloride is preferable over cement copper as catalyst for the following reasons. First of all, CuCl shows no induction period and it is active at 100% of the life of the Si mass bed. On the other hand, cement copper requires a long induction period and it is active at only 75% of the life of the Si mass bed. Furthermore, the finely divided cement copper powder is readily elutriated out of the Si mass bed during this induction period in a production-size reactor which normally operates at a linear gas velocity 20 to 30 times those observed in the one inch-diameter laboratory size reactor. Secondly, CuCl does not produce wasteful by-products since it reacts with Si metal to produce SiCl_4 and the needed catalytic species. On the other hand, the oxide-based cement copper is reduced by hydrogen under the reaction conditions to form water. The presence of water hydrolyses some chlorosilanes to form useless siloxane by-products.

C. Reaction Mechanism and the Nature of the Copper Catalyst

The effects of temperature, pressure and H_2/SiCl_4 concentration on the rate of the hydrochlorination reaction in the presence of a copper catalyst are similar to those observed without copper added. For example, Figure XIII shows the large temperature effect on the reaction rate at 300 psig and a H_2/SiCl_4 feed ratio of 1.0. At 60 seconds residence time, the conversion to SiHCl_3 is 17% at 400°C while 27% SiHCl_3 conversion is achieved at 500°C under similar conditions. The effect of reactor pressure on the reaction rate in the presence of copper is also similar to those observed

previously without copper. Figure XIV summarizes the experimental data on the effect of reactor pressure on the reaction rate at 500°C and $H_2/SiCl_4$ ratio of 2.8 with 5% CuCl initially added. At short residence times (less than 60 seconds), the reaction rate is somewhat slower at higher reactor pressure of 500 psig than those observed at lower reactor pressure of 300 psig. Here, the reaction rate is defined as the rate at which the hydrochlorination reaction reaches its equilibrium conversion to product $SiHCl_3$. The production rate in terms of pounds per hour of $SiHCl_3$ for a given reactor size is actually much higher at 500 psig than those achievable at 300 psig.

The plots in Figures III, IV, V, VI, VII and X show that, at long residence time, the % conversion to $SiHCl_3$ in the presence of copper appears to level off at about the same position as those observed from the same hydrochlorination reaction with no copper added. In other words, both kinetic curves, with and without copper, approach the same equilibrium conversion of $SiHCl_3$. In this respect, copper performs in the hydrochlorination reaction as a true catalyst since it changes the reaction rate but not the equilibrium composition.

The fact that an induction period is observed with cement copper while no induction period is noted for CuCl provides some experimental evidence on the nature of the copper catalyst. Since the oxide-based cement copper is rapidly reduced by hydrogen under the reaction conditions to elemental copper, the induction period can be explained as the time required for the "free" copper to form the active catalytic sites on the silicon metal surface. This also

points to the fact that free copper is not a catalyst in the hydrochlorination reaction of SiCl_4 and m.g. silicon metal to produce SiHCl_3 . However, once cement copper is activated, it shows about the same catalytic activity as that observed with CuCl . This suggests that a common catalytic species for the hydrochlorination reaction is formed on the silicon solid surface regardless what form of copper is used initially. Since Cu-Si alloys are known to be produced on the silicon metal surface (3) when CuCl reacts with Si under the reaction conditions, the active catalytic species must be the copper-silicon alloy. The elemental copper produced by the reduction of cement copper with hydrogen does not thermally form these copper-silicon alloys at the low reaction temperatures, $400^\circ\text{-}500^\circ\text{C}$. The elemental copper powder must go through a chemical transformation (most likely to copper chloride) so that the Cu-Si alloys can be produced through a chemical reaction. The induction period observed with cement copper is thus the time required for this chemical transformation to take place. On the other hand, cuprous chloride is a reactive chemical compound which readily reacts with silicon metal under the reaction conditions to form these Cu-Si alloys. Thus, no induction period is expected for CuCl .

The so-called copper-silicon alloys refer to the existence of Cu-Si metallic bonds. The mechanism of the hydrochlorination of SiCl_4 may be visualized as a first step chemisorption of SiCl_4 and/or hydrogen at the Cu-Si sites, viz.,

followed by the reduction of these activated $\text{Si} \cdots \text{Cl}$, $\text{Si} \cdots \text{Si}$ and $\text{Cu} \cdots \text{Cl}$ linkages to form SiHCl_3 and HCl . The HCl formed readily reacts with the Si at the Cu-Si catalytic sites to produce more SiHCl_3 according to the known reaction⁽²⁾,

As Si is consumed to form SiHCl_3 , the vacated site is filled by migration of Si atoms from the under-layers to regenerate the active Cu-Si species to complete the catalytic cycle of copper. This mechanism is very similar to the reaction mechanism of the well-known Direct Reaction between methyl chloride and silicon metal to produce methylchlorosilanes. The presence of these Cu-Si alloys is essential for the $\text{CH}_3\text{Cl} + \text{Si}$ reaction⁽³⁾. The above reaction mechanism suggests that the hydrochlorination of SiCl_4 to SiHCl_3 occurs on the solid silicon metal surfaces. Since HCl is known to readily react with Si metal at about 300°C , the intermediate HCl generated from the hydrochlorination of SiCl_4 would be instantaneously consumed by the surface Si atoms at these much higher reactions temperature of $400^\circ\text{--}500^\circ\text{C}$. In this respect, HCl may not exist as such in the gaseous phase in the Si mass bed. Since HCl gas is highly corrosive to metals at temperatures above 500°C , the existence or non-existence of a significant amount of "free" HCl in the hydrochlorination reactor could be the key factor in terms of corrosion.

D. Summary of Progress

Work on the JPL Government Contract No. 955 382 has progressed on schedule as outlined in the attached Program Plan. Two copper compounds (Cement Copper and Cuprous Chloride) have been evaluated as catalysts for the hydrochlorination reaction. Both copper catalysts show significant catalytic activity, approximately doubling the reaction rate. The effect of copper on the rate of the hydrochlorination reaction was measured as a function of reaction temperature, reactor pressure and $H_2/SiCl_4$ feed ratio. Results from the copper catalyst studies provide experimental evidence on the mechanism of the hydrochlorination reaction and on the nature of the active copper catalyst.

RECOMMENDATION

Results of the copper catalyst studies show that cuprous chloride is the preferred catalyst over the cement copper selected for the hydrogenation reactor of the Union Carbide, silane-to-silicon EPSDU. Although the presence of copper improves the reaction rate by about 100%, the application of copper depends on a number of factors including the reactor design and the mode of operating the hydrochlorination process. The presence of copper benefits the most when the hydrochlorination process is operated at high linear gas velocities (short residence times). On the other hand, minimal benefits of using copper can be realized if one operates the hydrochlorination process close to equilibrium conditions at long residence times, since both kinetic curves with and without copper approach the same equilibrium conversion of $SiHCl_3$.

PROJECTED FIFTH QUARTER ACTIVITIES

Planned activities for the fifth quarter (April - June) include,

- Continue copper catalyst studies at a lower CuCl concentration (2%)
- Study the effect of particle size distributions and surface areas on the rate of the hydrochlorination reaction
- Collect equilibrium data as a function of temperature

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TABLE I HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 500 PSIG,
500°C AND H_2/SiCl_4 RATIO OF 2.8 WITH 5% CEMENT COPPER

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole% ⁽²⁾		
			SiH_2Cl_2	SiHCl_3	SiCl_4
1	1735	34.9	1.005	30.06	68.91
2	1195	50.6	1.126	33.56	65.31
3	790	76.5	1.277	35.50	63.23
4	395	153	1.305	36.26	62.44
5	210	288	1.482	38.10	60.42

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE II HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 500 PSIG,
450°C AND H_2/SiCl_4 RATIO OF 2.8 WITH 5% CEMENT COPPER

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole% ⁽²⁾		
			SiH_2Cl_2	SiHCl_3	SiCl_4
1	1715	34.9	0.711	24.02	75.28
2	1105	54.2	0.856	29.06	70.09
3	657	91.2	0.968	31.88	67.16
4	390	154	1.148	33.86	64.99
5	193	310	1.290	35.79	62.92

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE III HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 300 PSIG,
500°C AND H_2/SiCl_4 RATIO OF 1.0 WITH 5% CEMENT COPPER

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole% ⁽²⁾		
			<u>SiH_2Cl_2</u>	<u>SiHCl_3</u>	<u>SiCl_4</u>
1	1552	13.7	0.616	21.12	78.53
2	1158	18.3	0.622	21.72	77.66
3	705	30.1	0.719	23.67	75.61
4	382	55.5	0.792	27.02	72.19
5	187	113	1.049	29.18	69.77

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE IV HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 300 PSIG,
500°C AND H_2/SiCl_4 RATIO OF 2.8 WITH 5% CEMENT COPPER

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole% ⁽²⁾		
			SiH_2Cl_2	SiHCl_3	SiCl_4
1	1750	16.6	0.861	28.19	70.95
2	1288	22.6	0.969	29.91	69.13
3	690	42.1	1.125	33.06	65.82
4	386	75.4	1.416	35.21	63.37
5	150	194	1.626	38.06	60.31

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE V HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 500 PSIG, 500°C AND H_2/SiCl_4 RATIO OF 2.8 WITH 5% CUPROUS CHLORIDE

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole% ⁽²⁾		
			SiH_2Cl_2	SiHCl_3	SiCl_4
1	1780	44.9	1.404	34.13	64.47
2	1246	64.2	1.450	37.98	60.57
3	770	104	1.610	39.23	59.16
4	370	216	1.977	41.28	56.74
5	237	338	2.271	41.38	56.35

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE VI HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 500 PSIG,
450°C AND H_2/SiCl_4 RATIO OF 2.8 WITH 5% CUPROUS CHLORIDE

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole% ⁽²⁾		
			SiH_2Cl_2	SiHCl_3	SiCl_4
1	1782	46.4	0.925	29.93	69.14
2	1244	66.5	1.240	32.88	65.89
3	692	120	1.504	35.32	63.18
4	382	216	1.446	38.92	59.63
5	222	373	2.074	39.39	58.54

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE VII

HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 300 PSIG,
500°C AND H_2/SiCl_4 RATIO OF 1.0 WITH 5% CUPROUS CHLORIDE

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole% ⁽²⁾		
			SiH_2Cl_2	SiHCl_3	SiCl_4
1	1550	18.2	0.461	21.86	77.68
2	1037	27.2	0.574	23.63	75.81
3	700	40.2	0.923	26.55	72.53
4	390	72.2	0.944	28.64	70.42
5	147	192	1.311	31.02	67.68

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE VIII HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 300 PSIG,
400°C AND H_2/SiCl_4 RATIO OF 1.0 WITH 5% CUPROUS CHLORIDE

Experiment No.	Hydrogen Feedrate SCCM ⁽¹⁾	Residence Time Second	Reaction Product Composition mole% ⁽²⁾		
			<u>SiH_2Cl_2</u>	<u>SiHCl_3</u>	<u>SiCl_4</u>
1	1908	18.3	0.078	9.91	90.02
2	1406	24.8	0.100	11.42	88.49
3	789	44.1	0.189	15.94	83.88
4	458	76.0	0.277	19.09	80.64
5	254	137	0.435	21.92	77.65
6	135	258	0.599	25.90	73.50

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

FIGURE 1 Apparatus For The Hydrogenation Of SiCl_4 To SiHCl_3

FIGURE II HYDROCHLORINATION OF SiCl_4 AT 300 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 1.0$ WITH 5% CEMENT COPPER CATALYST

WITH CEMENT TYPE COPPER AND INDUCTION PERIOD OF 15-20 HOURS WAS OBSERVED

FIGURE III

HYDROGENATION OF SiCl_4 AT
500 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 2.8$
WITH AND WITHOUT COPPER CATALYST

FIGURE IV HYDROCHLORINATION OF SiCl_4 AT 500 PSIG, 450°C AND $\text{H}_2/\text{SiCl}_4 = 2.8$ WITH AND WITHOUT COPPER CATALYST

FIGURE V HYDROCHLORINATION OF SiCl_4 AT 300 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 1.0$ WITH AND WITHOUT COPPER CATALYST

FIGURE VI HYDROCHLORINATION OF SiCl_4 AT 300 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 2.8$ WITH AND WITHOUT COPPER CATALYST

FIGURE VII

HYDROCHLORINATION OF SiCl_4 AT
300 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 1.0$
WITH 5% CuCl CATALYST

"REACTIVE" CuCl CATALYST SHOWED
ESSENTIALLY NO INDUCTION PERIOD

FIGURE VIII HYDROCHLORINATION OF SiCl_4 AT 500 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 2.8$ WITH AND WITHOUT COPPER CATALYST

FIGURE IX

HYDROCHLORINATION OF SiCl_4 AT
500 PSIG, 450°C AND $\text{H}_2/\text{SiCl}_4 = 2.8$
WITH AND WITHOUT COPPER CATALYST

FIGURE X HYDROCHLORINATION OF SiCl_4 AT 300 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 1.0$ WITH AND WITHOUT COPPER CATALYST

FIGURE XI HYDROCHLORINATION OF SiCl_4 AT
300 PSIG, 400°C AND $\text{H}_2/\text{SiCl}_4 = 1.0$
WITH AND WITHOUT COPPER CATALYST

FIGURE XII

HYDROCHLORINATION OF SiCl_4 AT
300 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 1.0$
WITH AND WITHOUT COPPER CATALYST

FIGURE XIII

EFFECT OF REACTION TEMPERATURE
ON REACTION RATES AT 300 PSIG
AND $H_2/SiCl_4 = 1.0$ WITH 5% $CuCl$

FIGURE XIV

EFFECT OF REACTOR PRESSURE ON
THE REACTION RATE AT 500°C
AND $H_2/SiCl_4 = 2.8$ WITH 5%
CEMENT COPPER

Year
Month of Year
Month of Contract

1979												1980												1981		
4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3			
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24			

I	Program Plan, Laboratory Site Preparation
II	Finalize Reactor Design, Order Equipment
III	Construct Hydrogenation Apparatus
IV	Safety Review, Start-Up, Standardization

1		
1-2		
2-3-4-5		
5		

V Process Studies

A. Reaction Kinetics

- (1) Function of T,P,H₂/SiCl₄: with no Catalyst
- (2) Establish Rate Equation, Reaction Order
- (3) Copper Catalyst Studies: T,P,H₂/SiCl₄
- (4) Particle Size Distribution, Surface Area
- (5) Different Grade of MG Si

B. Mass Life Studies

- (1) With no Catalyst Added
- (2) With Cu Catalyst Added
- (3) Different Grade of MG Si

▲	▲	▲	
5 6 7 8			
8 9			
8 9 10 11 12 13			
	13 14 15		
	14 15 16		
		16 17 18	
		18 19 20	
		20 21 22	

- VI Research and Development**
 - A. Method of Preparing Cu/Si Mass**
 - (1) Literature Studies
 - (2) Prepare Cu/Si Mass
 - (3) Evaluation and Optimization
 - B. Reaction Mechanism Studies**
 - (1) Literature Studies
 - (2) Identify Reaction Intermediates: HCl, etc.
 - (3) Identify Intermediate Reaction Steps
 - (4) Nature of the Equilibrium Reactions
 - (5) The Role of Copper Catalyst
 - a. Nature of the Catalytic Sites
 - b. Copper Transport Mechanism
 - c. Copper Distribution on Solid Si Surfaces
 - (6) Kinetic Isotope Effect
 - C. Other Hydrogenation Catalysts**

▲	▲	▲	
1 2 3 4 5 6 7 8			
5 6 7 8			
8 9 10 11 12 13			
1 2 3 4 5 6 7 8			
6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21			
6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21			
6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21			
8 9 10 11 12 13 14 15			
8 9 10 11 12 13 14 15			
8 9 10 11 12 13 14 15			
	▲		22 23
	▲		22 23

VII Reports

- A. Recommendation on Optimum Reaction Conditions
- B. Recommendation for Additional Development Work
- C. Final Report

9	14	19	23
9	14		23
			23 24

▲ Milestone Check Points