

## Discovery of Tin and Phosphorus Effects on the Direct Synthesis of Methylchlorosilanes

Larry H. Wood,

Dow Corning Corporation, 4770 Highway 42 East, Carollton, KY 41008

Concurrent with the commercialization of the copper catalyzed Direct Process Reaction of methyl chloride with silicon, research efforts got underway not only to explore what new products could be made and sold, but how to make those products more economically. While the direct process reaction was a significant improvement over the Grignard process, the yields to desirable products were dismal when compared to today's standards. Much of this poor performance was due to the quality of silicon and copper raw materials used by the industry. Initial process development work was done with ferrosilicon and with copper whose purity was only 95-96%. Much of the focus at the time was on just getting the silicon to react, and there was much effort to discover better initiation parameters such as HCl addition and temperature. The progress in the field was hampered by a lack of a fundamental understanding of the chemistry of the reaction, and much of the improvements made were simply finding a better source of copper and a better source of silicon with minor tweaks in the process. At the same time, changing commercial reactor design complicated the picture as the fluidized bed reactor replaced the tumbling bed reactor. . In addition, the desirable product from the reaction has not been consistent. While  $\text{MeSiCl}_3$  has always been undesirable, at times it was advantageous to suffer an increase in the  $\text{MeSiCl}_3$  produced and a decrease in the  $\text{Me}_2\text{SiCl}_2$  in order to maximize the  $\text{MeHSiCl}_2$ . As can be expected, this led to much confusion when identifying what a "good" run was compared to a "bad" run, and contributed not a little to confusion in the ongoing research efforts.

As with practically all the other additives evaluated, tin and phosphorus have been seen as positive by some researchers and negative by others. This is undoubtedly due to the changing picture as to the quality of the silicon raw material and the copper catalyst. Few of the silicon and copper impurities were suspected to have the kind of impact on the Direct Process reaction, at the levels they were present, as is observed today.

Of tin and phosphorus, tin was the first observed to affect the Direct Process reaction significantly. At Dow Corning, Robert Rownd first recorded the effect of tin in 1950, as he began studying the effects of additives to an experimental fluidized bed reactor. Then he reported the characteristic reduction of SiH containing chlorosilanes such as  $\text{MeHSiCl}_2$  and  $\text{HSiCl}_3$ , though this was considered somewhat as a negative, as it was desirable to maximize  $\text{MeHSiCl}_2$  at that time. Dow Corning was obviously not alone in the search for beneficial additives as, in 1951, Hoshino and Kojima, of the Tokyo Institute of Technology, received a patent on the use of tin(II) chloride as a treatment of silicon to increase the yields of  $\text{Me}_2\text{SiCl}_2$ . Throughout the 50's and 60's, experiments were conducted in laboratory scale reactors by Don Vallender and David Thomas to determine the optimum levels of tin to add depending on the desirable product distribution at the time. Since the effect of tin was so significant at such low levels, it was suspected that there was likely an interaction between tin and other impurities/additives

that could be capitalized upon. Subsequently, Ken Moorhead continued designed experimental studies in the 1970's using stirred bed reactors, and included tin in his study of the effect of various additives to the Direct Process reaction. The importance of tin to both reactivity and product distribution was confirmed.

During these development efforts, the characteristic effect of tin increasing the Direct Process Residue was observed as well as the negative impact that too much tin has on silicon conversion. The levels of added tin have changed little since the commercial reactors have been optimized for the production of  $\text{Me}_2\text{SiCl}_2$ . However, the reason that a few tens of ppm of tin can have such a large impact on the reactivity and product distribution is still not understood.

Like tin, phosphorus has been investigated since the early 1950's. When first added as phosphorus trichloride to the Direct Process Tumbler reactors, little effect was observed. Phosphorus has been reported by other researchers since that time to be both a promoter and a poison to the Direct Process reaction. The different conclusions concerning the effect of phosphorus on the Direct Process reaction were likely due to the varying techniques used to add phosphorus to the reaction contact mass, as well as other additives/impurities present in the silicon raw material and copper catalyst.

The effort at Dow Corning which led to the conclusive discovery that phosphorus could be used to improve the product distribution from the Direct Process reaction began as a program to control the species in the metallurgical grade silicon with the goal of increasing the efficiency of the reaction with methyl chloride. A new silicon refining technology was found by a team of Dr. Roland Halm, Ollie Wilding, and Regie Zapp to produce silicon that gave better performance in the Direct Process than silicon refined by the conventional techniques of chlorine or oxygen gas blowing. Dr. Robert Smith was called upon to identify differences in the silicon refined by the different techniques to see if the cause of the improvements could be discovered. Though it was at the limits of the DC arc emission analytical technique he was using, he was able to identify an increase in phosphorus in the silicon refined by the new technology as compared to that refined by the conventional technology. Phosphorus had been unknowingly added to the silicon. This led to the discovery that a processing aid in the new technology had tricalcium phosphate added to it as an anti-caking additive.

A hypothesis was developed to explain how phosphorus could be present in the silicon metal. The vapor pressure of elemental phosphorus indicated that it was not possible for it to exist in solution at the levels indicated. It was proposed that a phosphorus compound was formed from the reduction of the tricalcium phosphate by the molten silicon metal which had a vapor pressure low enough that at molten silicon temperatures it could remain in the silicon at concentrations above 100 ppm. Thermodynamic calculations indicated that the reduction of tricalcium phosphate by silicon to calcium phosphide ( $\text{Ca}_3\text{P}_2$ ) was possible. Calcium phosphide has a boiling point of  $1540^\circ\text{C}$ .

Alloying experiments were subsequently carried out in a laboratory furnace to test this hypothesis via the addition of calcium phosphide to molten silicon. These experiments

were successful in obtaining the dramatic improvement in the Direct Process selectivity that had been observed earlier. It was then proposed that this phosphorus species might also improve the selectivity of the Direct Process reaction simply by adding it directly to the ground silicon used in the reaction instead of going through the alloying step.

Evaluation of the addition of calcium phosphide to the Direct Process reaction contact mass in the Vibrating Bed Reactors (VBR's) demonstrated that the improvement in selectivity towards  $\text{Me}_2\text{SiCl}_2$  could be achieved by its addition as a powder as well as by being alloyed into the silicon. It was observed as well to have a negative impact on silicon conversion.

Because of the negative effect on silicon conversion and the handling difficulties of  $\text{Ca}_3\text{P}_2$ , experimentation was shifted to identifying alternative phosphorus compounds, which would give similar beneficial effects. Numerous compounds were evaluated. Oxygen containing compounds of phosphorus were found to be ineffective or detrimental to the reaction. A number of metal phosphides was identified which give the desired selectivity enhancement and copper phosphide was chosen for application on the commercial scale.

One may ask what those factors were that have impeded progress in the identification of the "best" catalyst package for the Direct Process reaction. One of the chief of these factors has been the inability to see signals above the noise of the process. In the commercial processes the fluid bed reactors are still not run in a consistent manner. Not only are these reactors run differently in different companies, but they are run differently in the different sites within a company, the different fluid beds of a site, and even differently by the different operators of a single reactor. The variability caused by these differences many times mask the differences caused by different silicons being reacted and the different catalytic packages being added. Improvements in the consistency of operation of the reactors are being made, and this has resulted in new signals above the noise. This same problem affects laboratory experimentation. The variability of results seen in the laboratory reactors, whether they be Fixed Bed Reactors, Vibrating Bed Reactors, Stirred Bed Reactors, or Fluid Bed Reactors have, in many cases, been worse than that observed in commercial scale reactors. Dow Corning has been fortunate to have essentially one person running the laboratory scale reactors for the past 20 years. This has given us the opportunity to achieve a degree of precision that has allowed us to see signals not seen before. It could well be said that the discovery of the benefits of phosphorus addition could have been delayed for a number of years if we had not the precision in the running of our laboratory reactors which we then did. It is my belief that the next step change improvement in the operation of the FBR's will be as a result of operating the reactors, both commercial and laboratory, in a more consistent and repeatable fashion.