PREPARATION OF SILICON TETRACHLORIDE

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William Richard Barnes, Knutsford, and Harold Garton Elean, ... of FIGURE I in which the reflectors 4 and 5 are combined into one unit and, instead of being elliptical, are parabolic.

FIGURE I shows a perspective view of part of an apparatus for preparing silicon tetrachloride in accordance with the invention, and FIGURE II shows a similar view of another form of the apparatus shown in FIGURE I.

In FIGURE I, reference 1 indicates a horizontal silica tube at one end of which is provided an inlet tube 2 and at the other end an outlet tube 3. The tube 1 is surrounded by a metallic reflector structure constituted by two similar elongated cylindrical reflectors 4 and 5, each having a transverse cross-section in the form of an arc of an ellipse; the reflectors are arranged relative to one another in such manner that they have a common focal line. In the drawing the reflectors 4 and 5 are shown partly broken away, the continuation of the parts broken away being shown by broken lines. The tube 1 is arranged within the reflector structure with its axis substantially coincident with the common focal line of the elliptical reflectors 4 and 5. At the other focal lines of the reflectors 4 and 5, are arranged tubular ultra-violet lamps 6 and 7, respectively. The reflector structure 4, 5 is therefore adapted to focus ultra-violet light emitted by the lamps 6 and 7 onto the tube 1, which tube is transparent to the ultra-violet light. Within the tube 1 is a mass of finely divided ferrosilicon alloy (not shown); suitable alloys are those containing from 10 to 70% or even more of iron, the balance being silica so far as traces of impurities which are normally present in ferrosilicon alloys such as, for example, carbon, aluminium and calcium. The alloy should be finely divided for example sufficiently finely divided to pass a 60 mesh British standard sieve, which sieve has apertures of width 0.2511 mm.

Using the apparatus described above the process of the invention was carried out as follows. Chlorine gas was introduced through the inlet tube 2 and irradiated by ultra-violet radiation from the lamps 6 and 7. The silicon tetrachloride produced as the gas passed over and reacted with the ferrosilicon alloy flowed through the outlet tube 3 and was condensed in known manner (not shown).

By carrying out the process as described and illustrated it was found unnecessary to supply to the reaction tube 1 a source of heat other than that produced by the ultra-violet lamps 6 and 7. Employing for each of the lamps 6 and 7 a 400 watt mercury vapour lamp, the reaction proceeded satisfactorily and the temperature of the ferrosilicon mass was estimated to be about 75 to 80°C.

FIGURE II shows apparatus similar to that of FIGURE I in which the reflectors 4 and 5 are combined into one unit and, instead of being elliptical, are parabolic.

The ultraviolet lamps 6 and 7 are positioned at the foci of the parabolic reflectors each of which reflects the radiation from the corresponding lamp as a parallel beam onto the reaction tube 1. This construction enables a reaction tube 1 of greater diameter to be employed. The tube 1 may be made of materials other than silica, such as a borosilicate glass, provided it is transparent or substantially transparent to the ultra-violet radiation employed.

The effect on the heterogeneous gas/solid reaction between the chlorine and the ferrosilicon alloy, of irradiating the chlorine with ultra-violet light was considerable and unexpected. When irradiation was omitted it was found necessary to heat the ferrosilicon alloy to at least about 300°C to obtain a satisfactory reaction rate. Even at this temperature, the reaction did not begin for some considerable time, the induction period often being an hour or more, which was a considerable inconvenience as the chlorine passing over during this induction period was wasted. However, by irradiating the chlorine with ultra-violet light in accordance with the invention the reaction occurred at a very much lower temperature and a substantial reduction in the induction period was obtained. A further advantage of the process of the invention which was obtained when ferrosilicon alloy was employed was that there was a considerable reduction in the amount of by-product ferric chloride sublimed over with the silicon tetrachloride because of the low operating temperature; in most cases the silicon tetrachloride obtained was virtually free of ferric chloride.

Instead of using an alloy of iron and silicon, an alloy of silicon and copper may be used. Furthermore, the silicon alloy may be replaced by a metal silicide such as magnesium, calcium or barium silicides.

The process of the invention may be employed to start a conventional silicon tetrachloride furnace; by employing ultra-violet radiation the induction period is very much reduced. Once the reaction has been started the radiation may be discontinued and the process carried on in the normal known way by heating the silicium-containing material to a suitable temperature.

Experiments will now be described illustrating the advantages obtained by irradiating the chlorine in accordance with the invention.

Experiment 1

Using the apparatus shown in FIGURE I, dry chlorine was passed over finely-divided ferrosilicon alloy containing 70% iron in silica tube 1 of diameter about 4 cms. The alloy was sufficiently finely-divided to pass a 60 mesh British standard sieve. The chlorine as it passed over the ferrosilicon alloy was irradiated with ultra-violet light from two 400 watt mercury vapour lamps 6 and 7. The induction period was about 10 to 15 minutes and the reaction temperature of the mass of alloy was about 75-80°C. The production rate of silicon tetrachloride was 13.4 g. per hour. The silicon tetrachloride product obtained was yellow in colour and was substantially free of iron chloride. To remove the dissolved chlorine it was necessary merely to heat the product under reflux when a clear liquid was obtained.

Experiment 2

To show the effect of the irradiation, a similar experiment was performed without irradiating the chlorine.

The ferrosilicon was heated in the dark to a temperature of 280°C to start the reaction. In this case, the induction period was about 34 hours. The rate of production of silicon tetrachloride, once begun, was the same as in the previous experiment. The product obtained was, however, brown in colour due to the presence of appreciable amounts of ferric chloride. To obtain a
pure product it was necessary to distill off the silicon tetrachloride from the crude mixture, dissolved chlorine being also removed in this operation.

What is claimed is:

1. A process for preparing silicon tetrachloride in which chlorine gas irradiated with ultra-violet light is reacted with a finely divided silicon-containing material selected from the group consisting of metal alloys of silicon and metal silicides at a temperature not greater than 300° C. to produce silicon tetrachloride.

2. A process as claimed in claim 1, in which the heat required to heat the reactants to a temperature at which reaction occurs is provided by the source of ultra-violet radiation.

3. A process as claimed in claim 1, in which after the reaction between chlorine and silicon alloy has started, the irradiation is stopped and the reactants heated to a suitable higher temperature at which the reaction can continue in the absence of the radiation.

4. A process as claimed in claim 1 in which the silicon-containing material employed is ferrosilicon.

5. A process as claimed in claim 1, in which the ultra-violet radiation is provided by a mercury vapour lamp.

References Cited in the file of this patent

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