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PREPARATION OF ORGANO-HALOGENO-SILANES

Harold Garton Emblem, Grappenhall, and Richard Charles Le Fleming, Huyton, near Liverpool, England, assignors to Philadelphia Quartz Company, Philadelphia, Pa., a corporation of Pennsylvania

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This invention relates to processes for the preparation of organo-halogeno-silanes, and more particularly relates to the preparation of such compounds by processes in which a compound of the formula RX , where R is an alkyl group and X is a halogen atom, is reacted at an elevated temperature with a silicon-containing contact mass.

Reactions of this kind are known in which it has been proposed to use a ferrosilicon alloy as the supply of silicon. It is also known that such reactions are catalysed by copper and contact masses have been prepared by fusing ferrosilicon with copper to produce a silicon-copper-iron alloy. However, it is not easy to prepare active silicon-copper-iron alloys by fusion and great care is necessary if good and reproducible results are to be obtained. Furthermore, to obtain satisfactory results, the initial ferrosilicon alloy must be one of low iron content, and it is preferably one containing less than 25% by weight of iron.

It is an object of the present invention to provide a relatively simple process for preparing a contact mass, for reaction with an alkyl halide to prepare alkyl halogeno-silanes, employing as a starting material a ferrosilicon alloy. It is a further object of the invention to provide a process for preparing alkyl halogeno-silanes employing such contact masses.

The present invention provides a process for the preparation of a contact mass for reaction by heating with an alkyl halide to prepare alkyl halogeno-silanes, and is based on the discovery that an active contact mass can readily be prepared from a ferrosilicon alloy containing more than 50% by weight of iron, by treating the alloy in a finely-divided state with an aqueous solution of a water-soluble cupric salt to replace part of the iron present in the alloy by copper.

The treatment of the ferrosilicon alloy is conveniently effected by stirring the finely-divided alloy in a copper salt solution maintained at a raised temperature, for example 60° to 80° C. The said alloy and manner of treatment are preferably such that the alloy after treatment contains at least 5% by weight of copper, more preferably at least 10%. The alloy preferably contains prior to treatment at least 65% by weight of iron.

Examples of suitably cupric salts that can be used in the process of the invention are the chloride, nitrate and sulphate.

The aqueous solution of the water-soluble cupric salt is preferably acidified although the acid chosen for this purpose should not be such that it prevents or hinders the replacement of the elemental iron contained in the alloy by copper in accordance with the invention; thus the acid should not dissolve to any appreciable extent the copper introduced into the alloy or form insoluble or sparingly soluble copper compounds such as cupric fluoride. Hydrofluoric acid, for example is thus unsuitable for this purpose. It may be mentioned that even if the undesirable formation of insoluble cupric fluoride were overcome by the addition of excess hydrofluoric acid to solubilise the cupric fluoride, the use of this acid would still be objectionable because the acid might cause dissolution of any free silicon in the alloy with the simultaneous deposi-

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tion of copper on the alloy and this is an effect not aimed at by the present invention.

Suitable acids for the acidification of the aqueous cupric salt solution are hydrochloric acid and sulphuric acid.

The process of the invention enables contact masses to be prepared in a simple manner from ferrosilicon alloys of high iron content, for example from such alloys containing 70% or even more by weight of iron, the balance being silicon and traces of impurities such as carbon, aluminium, calcium and other metals which are normally present in commercial ferrosilicon alloys.

The present invention also provides a process for preparing alkyl halogeno-silanes by reacting at an elevated temperature a contact mass prepared in accordance with the invention with an alkyl halide. The preferred contact masses are those containing 20% or more by weight of silicon.

The reaction may be carried out in the usual manner by passing the alkyl halide vapour over the contact mass heated to 200° to 500° C., for example from 300° to 400° C. The reaction may be carried out in a silica or mullite tube in a furnace. The reaction products issuing from the reaction vessel are condensed and then, if desired, fractionated. The alkyl halide may be a saturated alkyl chloride, bromide or iodide; of these methyl and ethyl chlorides are preferred. Unsaturated alkyl halides, however, such as vinyl chloride may also be used.

The invention is illustrated by the following examples of which Examples 1 and 3 describe the preparation of contact masses in accordance with the invention and Examples 2, 4 and 5 describe the preparation of alkyl chloro-silanes by reacting alkyl chlorides with contact masses obtained in accordance with the invention.

Example 1

Finely-divided ferrosilicon alloy containing 70% by weight of iron was stirred in a 10% solution of hydrochloric acid, the solution containing cupric chloride in an amount such that the weight of copper in the solution was equal to the weight of iron in the alloy. The solution was maintained, with stirring, at 70° C. for 6 to 7 hours. In this treatment the free iron in the alloy dissolved in the cupric chloride solution displacing the copper which replaced the dissolved iron in the alloy. Displacement of copper from a solution of a copper salt by iron is well known and occurs because the so-called solution pressure of iron (in both the ferrous and ferric states) is greater than that of copper. The copper-containing ferrosilicon powder obtained was filtered, washed and dried at 160° C. The final material had the approximate composition by weight of 43% iron, 26% silicon and 31% copper.

A variation of the above procedure is to stir at room temperature for 3 hours and to then complete the reaction by heating, with stirring, at 70° C. for 3 to 4 hours.

Example 2

100 g. of the copper-containing ferrosilicon alloy obtained by the method of Example 1 was charged in a silica tube placed horizontally in a furnace and heated to 350° C. Methyl chloride vapour was passed over the heated contact mass for 5½ hours at the rate of 4.6 litres per hour. The effluent gases from the reaction vessel were condensed and collected in a liquid nitrogen trap and subsequently fractionated. The fraction having a boiling range of -25° to 0° C. weighed 4.5 g. and consisted essentially of unreacted methyl chloride. A fraction weighing 2.0 g. had a boiling range of 0° to 25° C.; this fraction which contained both silicon and hydrolysable chlorine was probably dichlorosilane. A third fraction consisting of methyl chlorosilanes was obtained which weighed 22.9 g. and had a boiling range of 58° to 64° C.

Example 3

140 g. of ferrosilicon (70% iron), all passing a 100 mesh B.S.S. sieve (which has apertures of width 0.152 mm.) were suspended in a solution of 170 g. of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ crystals in a mixture of 100 ml. water and 300 ml. concentrated hydrochloric acid solution. The mixture was heated to 80° C. and maintained at this temperature, while stirring for 7 hours. At the end of this time the copper-containing ferrosilicon was filtered, washed with water, and dried at 120° C. before use. The contact mass obtained had the composition 46.3% iron, 26.7% silicon and 27.0% copper.

Example 4

185 g. of a contact mass prepared as described in Example 3 was charged into a silica tube and heated to 320° C. Methyl chloride vapour was passed over the heated contact mass for 7½ hours at the rate of 4.6 litres per hour. The effluent gases from the reaction tube were condensed and collected in a liquid nitrogen trap and subsequently fractionated. 21.6 g. of crude product were obtained of which the fraction having the boiling range of -30° to 25° C., consisting mainly of unreacted methyl chloride, had a weight of 13.1 g. A second fraction was obtained of weight 7.1 g. having a boiling range of 40° to 60° C.; this consisted of trimethyl chlorosilane $(\text{CH}_3)_3\text{SiCl}$ and some silicon tetrachloride SiCl_4 .

Example 5

The process described in Example 4 was repeated, this time carrying out the reaction at a temperature of 350° C. and for 6¼ hours. 90 ml. of crude reaction product were obtained of which the fraction having a boiling range of -25° C. to 0° C. had a volume of 60 ml. and consisted mainly of unreacted methyl chloride. A fraction having a volume of 20 ml. was obtained with a boiling range of 50°-60° C.; this fraction consisted mainly of trimethyl-chlorosilane $(\text{CH}_3)_3\text{SiCl}$ and some silicon tetrachloride SiCl_4 .

What is claimed is:

1. A process which comprises:

- (a) placing a ferrosilicon alloy in a finely divided state in a reaction zone,
- (b) said ferrosilicon alloy containing more than 50 percent by weight of iron,
- (c) treating said finely divided ferrosilicon alloy with an aqueous solution of a water-soluble cupric salt,
- (d) permitting said ferrosilicon alloy and said cupric salt to react together in said reaction zone long

enough for the cupric salt to replace part of the iron present in the alloy by copper,

- (e) recovering a contact mass comprising a ferrosilicon alloy and metallic copper,
- (f) contacting said contact mass with an alkyl halide to produce alkyl halogenosilanes.
2. A process according to claim 1 wherein said contact mass contains between about 43 and 46.3% iron; between about 27 and 31% metallic copper and between about 26 and 26.7% silicon.
3. A process for preparing a contact mass containing iron, silicon and copper which comprises:
 - (a) placing a ferrosilicon alloy in a finely divided state in a reaction zone,
 - (b) said ferrosilicon alloy containing more than 50 percent by weight of iron,
 - (c) treating said finely divided ferrosilicon alloy with an aqueous solution of a water-soluble cupric salt,
 - (d) permitting said ferrosilicon alloy and said cupric salt to react together in said reaction zone long enough for the cupric salt to replace part of the iron present in the alloy by copper,
 - (e) said contact mass being capable of being reacted with alkyl halides to produce alkyl halogenosilanes.
4. A process as claimed in claim 3, in which the alloy contains prior to treatment at least 65% by weight of iron.
5. A process as claimed in claim 3, in which the alloy after treatment contains at least 5% by weight of copper.
6. A process as claimed in claim 3, in which the alloy after treatment contains at least 20% by weight of silicon.
7. A process according to claim 3 wherein the final contact mass contains between about 43 and 46.3% iron, between about 27 and 31% metallic copper and between about 26 and 26.7% silicon.

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