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(54) ELECTROLYTIC PROCESS FOR THE PREPARATION
 OF PERFLUOROMETHYL IODIDE

(71) We, HOECHST AKTIEN-
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 organised according to the laws of the
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 Federal Republic of Germany, do hereby
 declare the invention for which we pray that
 a patent may be granted to us, and the
 method by which it is to be performed, to be
 particularly described in and by the
 following statement:—

The present invention relates to an
 electrolytic process for the preparation of
 perfluoroethyl iodide.

Together with tetrafluoroethylene,
 perfluoroethyl iodide is a useful starting
 material for the preparation of valuable
 fluorine compounds of relatively high
 molecular weight. Hitherto, it has generally
 been prepared by the reaction of iodine
 pentafluoride with iodine and
 tetrafluoroethylene. In this process the
 iodine pentafluoride must be prepared in a
 separate step from iodine and elementary
 fluorine; the transport and handling of
 elementary fluorine are, however,
 inconvenient. In an alternative process, it is
 possible to react elementary fluorine
 directly with tetrafluorodiiodoethane to
 give perfluoroethyl iodide. Attempts have
 also been made to prepare perfluoroethyl
 iodide in anhydrous hydrofluoric acid, while
 using other oxidising agents, for example,
 chloric or oxygen-containing acids.
 However, all these processes involve great
 corrosion problems.

It would therefore be desirable to prepare
 perfluoroethyl iodide without the use of
 other oxidising agents and especially
 without the use of elementary fluorine.

The present invention provides a process
 for the preparation of perfluoroethyl iodide,
 which comprises electrolysis of a liquid
 mixture of tetrafluorodiiodoethane and
 anhydrous hydrofluoric acid.

The electrolysis is preferably carried out
 at a voltage within the range of from 3 to 8.5
 volts.

The process is preferably carried out in an

electrolytic cell having a common anode 50
 and cathode chamber, for example, a
 Simons cell (see German Patent
 Specification No. 817 151 and U.S. Patent
 Specification No. 2 519 983).

As mentioned above, the electrolysis is 55
 preferably carried out at a voltage within
 the range of from 3 to 8.5 V, a voltage of
 from 4 to 6 V being especially advantageous.
 The electrolyte consists of a liquid mixture
 of tetrafluorodiiodoethane and anhydrous 60
 hydrofluoric acid. Its temperature is
 preferably not lower than -15°C ; and on
 the other hand, the pressure and
 temperature should be so chosen that the
 hydrofluoric acid is present in the liquid 65
 phase. The temperature preferably does not
 exceed 19°C .

The tetrafluorodiiodoethane used may be
 prepared by any suitable process. For
 example, a mixture of iodine and 70
 tetrafluorodiiodoethane may be reacted
 with tetrafluoroethylene in an autoclave,
 whilst stirring. The tetrafluorodiiodoethane
 acts as a solvent and promotes the reaction
 process. 75

The electrolysis cell should consist of
 materials stable towards hydrofluoric acid,
 for example, VA steels, nickel, copper and
 polypropylene. In order to increase the
 effective surface area for the electrolysis, 80
 the electrodes are advantageously designed
 as electrode bundles.

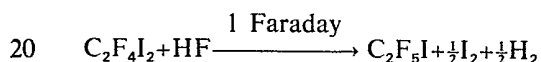
The distance between the anode and the
 cathode may vary within a wide range,
 distances within the range of from 1.5 to 85
 15.0 mm being advantageous. Distances
 within the range of from 3.0 to 6.0 mm are
 especially useful. The anode is
 advantageously made of nickel, and the
 cathode may also be made of this metal; 90
 other metals, for example iron, may also be
 successfully used for the cathode. For
 manufacturing reasons, the thickness of the
 electrode plates is preferably within the
 range of from 0.5 to 3 mm. 95

At low temperatures,
 tetrafluorodiiodoethane is practically
 insoluble in anhydrous hydrofluoric acid.

Agitation of the electrolyte is preferred in order to obtain an intimate mixture of the two substances. This also helps to prevent the deposition of the tetrafluorodiiodoethane and to establish the contact of this compound with the anode. It is, therefore, advantageous to provide for thorough stirring or for circulation by means of a pump in the cell.

In the case of circulation by means of a pump the flow direction is suitably so chosen that the electrolyte enters from below into the electrode interspaces and leaves the electrode space at the top. In this manner, the separation of the gaseous phases is facilitated.

The process of the invention may be described by the following reaction equation:



When the process is operated discontinuously, the proportion of tetrafluorodiiodoethane in the electrolyte naturally decreases with time, whereas the concentration of perfluoroethyl iodide increases, and iodine separates out.

The molar ratio of tetrafluorodiiodoethane to HF preferably does not exceed 1:1. A concentration in the range of from 2 to 25% by weight of tetrafluorodiiodoethane in the electrolyte is especially advantageous.

When the process is operated continuously, it is necessary to remove the iodine formed, for example, by filtration, either periodically or continuously. When this is done, the content of tetrafluorodiiodoethane is preferably not less than 10% by weight.

The composition of the electrolyte, the cell temperature and the geometrical data of the cell, for example, the electrode distance and the electrode thickness, all determine the electrical resistance of the electrolyte. This resistance, the voltage applied and the effective electrode surface area determine the current density (or current intensity). In relatively small apparatus, current density values of up to about 3 A per dm² of anode surface are obtained.

The process of the invention does not impose any particular requirements with respect to pressure, except that the hydrofluoric acid should be present as a liquid. For safety reasons it is advantageous to operate only at atmospheric pressure or slightly above atmospheric pressure, but in principle the process may also be carried out at high pressures. It is recommended in all cases to use a master pressure gauge and rupturable membranes, since fluorine

together with traces of water may form the explosive difluoroxide.

Tetrafluorodiiodoethane is insoluble in anhydrous hydrofluoric acid at low temperatures and would not, therefore, be expected to react. It was surprising that a suspension of tetrafluorodiiodoethane and hydrofluoric acid could be brought to reaction at all, and even more surprising that the reaction came to a stop at the stage of perfluoroethyl iodide formation.

The iodine liberated in the reaction separates out in the form of fully developed crystals. It may be removed from the electrolyte, for example, by filtration, either periodically or continuously during the electrolysis. It is also possible, however, to allow the iodine to remain as a deposit until the reaction has been completed, and then to drain the electrolyte off from the cell and remove the remaining iodine from the cell with water. The iodine obtained is pure and may be used, after the hydrofluoric acid has been washed out, for the preparation of tetrafluorodiiodoethane from tetrafluoroethylene and iodine.

Because of the difference in the boiling points of tetrafluorodiiodoethane (112 to 113°C) and perfluoroethyl iodide (11°C), the latter can be readily separated from the former. The boiling point of perfluoroethyl iodide is, however, very close to that of hydrofluoric acid (19°C). Nevertheless, it has been found that perfluoroethyl iodide may be successfully separated from hydrofluoric acid in small distillation columns. Moreover, it has been found that the iodine also present does not interfere with the distillation of the perfluoroethyl iodide either, in spite of its relatively high vapour pressure.

The process of the invention is thus preferably carried out at a temperature in the range of from +10 to +19°C, the perfluoroethyl iodide formed in the reaction advantageously being eliminated in the gaseous state. When operating in this way it is recommended that the electrolysis cell be provided with a reflux condenser, the cooling liquid of which is at a temperature at or below the temperature of the electrolysis cell. For example, if the electrolysis is carried out at a temperature in the range of from +5 to +10°C, the condenser is advantageously maintained at a temperature in the range of from -5°C to +8°C. If, however, the electrolysis temperature is +19°C, as may be the case, for example, when using a relatively small apparatus, the condenser is suitably maintained at a temperature in the range of from +5°C to +11°C.

In a larger apparatus, where heat is conducted away less efficiently, it may be necessary to use a relatively lower

condenser temperature, or, better, to provide relatively larger condensers. The perfluoroethyl iodide leaves the top of the reflux column in the gaseous state and is condensed in a cooling trap at a temperature below -10°C . The condensate is as clear as water and is practically free from hydrofluoric acid. Upon standing for some time, the perfluoroethyl iodide turns a slightly violet colour.

When the throughput is small, the separation of the hydrofluoric acid and the perfluoroethyl iodide in the reflux column may be so good that the cooling trap may be made of glass. With a larger throughput, it is advantageous to insert an absorption pipe for hydrofluoric acid between the top of the column and the cooling trap, which pipe may be filled, for example, with sodium fluoride.

The following Examples illustrate the invention. In Examples 1 and 2, test apparatus as described below was used.

Test Apparatus

The electrolytic cell used was made of stainless steel. Including a cooling jacket, its diameter was 15 cm and its height 20 cm. The tetrafluorodiiodoethane was introduced via a filling funnel, and the hydrofluoric acid was removed from a supply vessel for hydrofluoric acid. The top and bottom of the cell were connected by a conduit pipe, into which a vane-type pump had been inserted. Furthermore, a valve for draining the electrolyte was included in the pump circuit. Besides, the electrolyte level in the cell could be monitored by means of an "inspection glass" consisting of a thin-walled polytetrafluoroethylene tube. The volume of the electrolyte was about 1500 ml and was distributed around the pump circuit and the cell interior. The temperature in the cell was monitored by two thermometers, and temperature gauge tubes entered into the cell from above via polytetrafluoroethylene seals. Insulated electrical leads, too, entered the cell from above. The anode as well as the cathode were made of nickel and had been designed in the form of a bundle. The effective electrode surface of the anode and the cathode was 20 dm^2 in each case. The electrode distance was 3 mm, and the thickness of the individual electrode plates was 1 mm. The cell cover carried a master pressure gauge and a reflux condenser having a length of about 75 cm which was intended to keep the hydrofluoric acid back. The perfluoroethyl iodide formed in the electrolytic cell was not kept back in the reflux condenser, but passed in the gaseous state into a cooling trap and condensed there as a liquid. The cooling trap was cooled with acetone/dry ice. The reflux

condenser and the electrolytic cell were connected with two different cooling systems, the temperature of which could be chosen in each case. The cooling liquid used was ethanol. The cooling installations were of conventional design. At the top of the reflux condenser there was a rupturable membrane with a minimum pressure of response of 1.5 bar.

The electrolytic current was generated by a rectifier provided with a voltage stabiliser to avoid mains fluctuations.

The line voltage, the current intensity and the temperature were recorded for control by recording devices. The amount of electrical energy consumed was determined by means of an electric meter.

EXAMPLE 1

At a temperature of -10°C , 1400 g of anhydrous hydrofluoric acid and 30 g of tetrafluorodiiodoethane were introduced into the above-described test apparatus. At the beginning of the electrolysis, the voltage was established at 7.5 V, and upon reaching an operating temperature of from $+11$ to 15°C , it was adjusted to a value of from 5.2 to 5.4 V. The intensity of current observed was 10 A. At first, the temperature in the reflux condenser was -4°C , and after the reaction had started it rose to $+1$ to $+2^{\circ}\text{C}$. The experiment was carried on for about 19 hours. In this process, 225 Ah were consumed. From the cooling trap, 14.9 g of perfluoroethyl iodide were isolated, which corresponded to 72% of the theoretical yield (current yield 0.7%). The isolated perfluoroethyl iodide was analysed by gas chromatography and showed a degree of purity greater than 95% (area per cent in g.c.).

EXAMPLE 2

In a manner analogous to that of Example 1, 150 g of tetrafluorodiiodoethane and 1400 g of anhydrous hydrofluoric acid were introduced into the apparatus. The operating voltage was established at first at 8.1 V and was later on adjusted to 5.3 V. The intensity of current was 10A. The operating temperature of the cell was in the range of from 11 to 12°C , and that of the reflux condenser had a maximum of $+3^{\circ}\text{C}$. The experiment was carried out for 31 hours, and over this period 400 g of hydrofluoric acid were gradually added. The current consumption was 315 Ah. 81.9 g of pure perfluoroethyl iodide were obtained, corresponding to 78.5% of the theoretical yield. Furthermore, 34 g of iodine (93% of the theoretical yield) were obtained. The iodine was rinsed from the cell with water. Analysis by gas chromatography showed that the degree of purity of the perfluoroethyl iodide was 97%.

EXAMPLE 3

Use was made of a fluorination unit having a working volume of 40 l, the design, of which corresponded to the test apparatus described above. 38.7 Grams of anhydrous hydrofluoric acid and 5.63 kg of tetrafluorodiiodoethane were introduced.

The test temperature was initially 0°C, later rising to about +10°C. The electrolyte was circulated vigorously by a magnetically coupled centrifugal pump. The average temperatures of the condenser were in the range of from 15 to 18°C in the entry area and from 3 to 10°C in the exit area. The average voltage was 5.5 V. In order to guarantee an even level of liquid, a total of 5.6 kg of hydrofluoric acid were gradually added throughout the experiment. The electrolysis was carried on for 62 hours. The current consumption was 3011 Ah.

A total amount of 2689 g of crude perfluoroethyl iodide was obtained. The average degree of purity was about 95%. Thus, the yield was approximately 2550 g of pure product, which corresponded to 65.5% of the theoretical yield based on tetrafluorodiiodoethane or to a current yield of about 9%.

WHAT WE CLAIM IS:—

1. A process for the preparation of perfluoroethyl iodide, which comprises electrolysing a liquid mixture of tetrafluorodiiodoethane and anhydrous hydrofluoric acid.

2. A process as claimed in claim 1, wherein the electrolysis is carried out at a voltage in the range of from 3 to 8.5 V.

3. A process as claimed in claim 2, wherein the electrolysis is carried out at a voltage in the range of from 4 to 6 V.

4. A process as claimed in any one of claims 1 to 3, wherein the electrolysis is carried out at a temperature in the range of from -15 to +19°C.

5. A process as claimed in any one of claims 1 to 4, wherein the molar ratio of tetrafluorodiiodoethane to hydrofluoric acid does not exceed 1:1.

6. A process as claimed in claim 5, wherein the mixture of tetrafluorodiiodoethane and anhydrous hydrofluoric acid contains from 2 to 25 per cent by weight of tetrafluorodiiodoethane.

7. A process as claimed in any one of claims 1 to 6, carried out in a Simons cell.

8. A process as claimed in any one of claims 1 to 7, wherein a nickel anode is used.

9. A process as claimed in any one of claims 1 to 8, wherein the distance between anode and cathode is in the range of from 1.5 to 15.0 mm.

10. A process as claimed in claim 9, wherein the electrode distance is in the range of from 3 to 6 mm.

11. A process as claimed in any one of claims 1 to 10, wherein the thickness of the electrodes is in the range of from 0.5 to 3 mm.

12. A process as claimed in any one of claims 1 to 11, wherein the electrolyte is agitated.

13. A process as claimed in claim 12, wherein the electrolyte is circulated by means of a pump.

14. A process as claimed in claim 13, wherein the electrolyte is so circulated that it passes upwardly through the space between the anode and the cathode.

15. A process as claimed in any one of claims 1 to 14, wherein the iodine formed in the reaction is periodically or continuously removed.

16. A process as claimed in claim 15, wherein the mixture of tetrafluorodiiodoethane and hydrofluoric acid contains not less than 10 per cent by weight of tetrafluorodiiodoethane.

17. A process as claimed in any one of claims 1 to 16, wherein the electrolysis is carried out at a temperature in the range of from 10 to 19°C and the perfluoroethyl iodide formed is removed in the gaseous state.

18. A process for the preparation of perfluoroethyl iodide, carried out substantially as described in any one of the Examples herein.

19. Perfluoroethyl iodide whenever prepared by a process as claimed in any one of claims 1 to 18.

20. Iodine whenever prepared by a process as claimed in any one of claims 1 to 18.

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