

UNITED STATES PATENT OFFICE.

HERMANN HABERLAND AND WALTER SCHAEFER, OF ZSCHERNDORF, GERMANY, AS-
SIGNORS TO THE FIRM OF SALZBERGWERK NEU-STASSFURT UND THEILNEHMER,
OF ZSCHERNDORF, GERMANY.

PROCESS OF MAKING PENTA- AND HEXA-CHLORETHANES.

1,036,224.

Specification of Letters Patent. Patented Aug. 20, 1912.

No Drawing.

Application filed February 24, 1912. Serial No. 679,700.

To all whom it may concern:

Be it known that we, HERMANN HABERLAND, a subject of the King of Prussia, and WALTER SCHAEFER, a subject of the King of Saxony, both residing at Zscherndorf, district of Bitterfeld, Germany, have invented certain new and useful Improvements in Processes of Making Penta- and Hexa-Chlorethanes; and we do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

Hexachlorethane has heretofore been technically produced by Faraday's reaction of chlorin on perchlorethylene.

Attempts to commercially manufacture hexachlorethane from a starting material cheaper than perchlorethylene have, up to the present, so far as known by us, not come into use.

Tetrachlorethane (acetylenetetrachlorid) has first been used by us to form perchlorethylene, which has heretofore been obtained indirectly from tri- and penta-chlorethane.

According to Mouneyrat (*Bulletin Société Chim.*, Paris (3) 19. 182, 454; and *Chem. Centralblatt*, Berlin 98. I, 883; II. 175) hexachlorethane results from the energetic chlorination of tetrachlorethane (acetylene tetrachlorid) by means of aluminium chlorid acting as a chlorin carrier at a temperature of 120° C.

The Salzbergwerk at Neu-Stassfurt, Germany, (German Patent 174068) reacts with chlorin on a mixture of tetrachlorethane, sulfur chlorid and iron powder, the latter acting as a contact substance. The reaction is carried out at a high temperature.

The use of a chlorin carrier, which must be used in large quantities, the comparative slowness of the reaction, the permanent maintenance of elevated temperature, the unavoidable separate purification of the final product, and the working up again of the contact substances have prevented the commercial manufacture, as the costs thereof are prohibitive to the production of a commercial product.

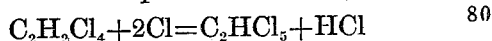
The following process completely avoids all the foregoing difficulties and effects a direct combination or reaction that proceeds

smoothly and results in a quantitative yield of pure hexachlorethane with the simultaneous production of hydrochloric acid as a by-product that is free from impurities.

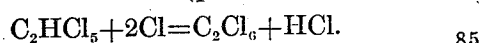
We have discovered that when tetrachlorethane is subjected to the action of chlorin gas in the presence of actinic rays from a source of artificial light it is converted with extraordinary rapidity into hexachlorethane without the use of a chlorin carrier or reagent.

The light to which the tetrachlorethane is subjected may be produced by an unenvolved or free arc lamp, a mercury vapor lamp, or other similar source of artificial light during the admission of the halogen, care only being taken to keep the high heat of reaction down, for example, to between 50° and 60° C., by a suitable cooling agent, so as to prevent the products from distilling over, or from sublimation while the hydrochloric acid gas that is produced in large quantities is condensed or absorbed in a suitable apparatus.

The tetrachlorethane is immediately transformed into pentachlorethane,

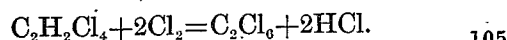


and the pentachlorethane is then converted into hexachlorethane (perchlorethane)



It will therefore be seen that penta-chlorethane can be produced by this process. In order to do so the reaction must be stopped at a suitable time, and advantageously as soon as about 10% in excess of the theoretical quantity of halogen has been supplied to the tetrachlorethane. The separation of the mixture of about 90% pentachlorethane and 10% hexachlorethane is done by fractional distillation or they may be separated by distilling the hexachlorethane, that has hardened in the cooler, with steam.

If hexachlorethane is desired, the reaction is carried on until the molecule is saturated with the halogen, namely until the theoretical quantity of chlorin has entered into the reaction and replaced all the hydrogen in the radical, as follows:



After the above-mentioned mixture has

been formed the hexachlorethane begins to separate in time from the mixture and after starting to separate, its formation and precipitation is very rapid. As soon as the liquid in the reaction vessel becomes thick and mushy the supply of chlorin is stopped, the white crystals are pressed to squeeze out the adhering liquid, to which is added a further quantity of tetrachlorethane for the formation of a new quantity of the product.

The process may be carried out continuously by withdrawing a portion of the reaction mass and replacing it with tetrachlorethane and then cooling that portion which has been removed, whereupon the greater part of the hexachlorethane held in solution will separate; it is then filtered and the filtrate returned to the reaction vessel. The hexachlorethane is therefore obtained directly, and pure.

The process is carried out commercially for instance by placing 300 kilos of tetrachlorethane in a vessel capable of resisting the action of chlorin and containing in its interior a Uviol mercury vapor lamp of suitable length, or any other source of artificial light. A rapid stream of chlorin is then admitted, and the rapidly rising temperature is kept down by water cooling to about 60° C. The large quantity of hydrochloric acid gas is allowed to pass into a suitable absorber containing water, or into a Riesel tower *e. g.* of the kind of washing towers, scrubbers or the like for absorption or condensation. The hydrochloric acid gas, free from water may be led off and directly used for any purpose. After supplying 200 kilos of chlorin, at the end of about fourteen hours the thick mush of hexachlorethane is formed and the reaction is completed. The pentachlorethane is then pressed out and the crystals are washed with tetrachlorethane. The resulting hexachlorethane is pure white and melts at 183°-184° C., with simultaneous sublimation. The yield corresponds to the theoretical quantity of chlorin required for the formation of the product, and there is no admixture of by-products.

Faraday observed that hexachlorethane was formed when dichlorethylene and chlorin were subjected to the action of sunlight. The commercial production by such a method is out of the question on account of

the great cost of the starting material and the dependence on sunshine.

The present process utilizes the cheap tetrachlorethane obtainable on the market in large quantities as a commercial product and by the use of artificial sources of light it is independent of external conditions, whereby its technical value in combination with practical simplicity of the process is alone established.

Artificial light has heretofore been only used in producing di- and tetra-chloracetylene (German Patents Lidholm 201705 and 204516, and Chemischen Fabrik Griesheim-Elektron, 204883); these processes, however, give no idea for the further chlorination of the products, and Patent 204883 states that an excess of chlorin produces tetrachlorethane without any additional products. The patents to Lidholm state that the source of light must be constant, or approximately so, to avoid explosions.

Penta- and hexa-chlorethane are formed in accordance with our process without danger of explosions or the requirement that the source of light be kept constant. The reaction takes place in the liquid, while the processes in the patents referred to require the treatment of a gaseous mixture that must be maintained in definite proportions.

We claim—

1. The process of chlorinating tetrachlorethane which comprises reacting on tetrachlorethane with chlorin gas in the presence of light capable of promoting chemical action.

2. The process of chlorinating tetrachlorethane which comprises reacting on tetrachlorethane with chlorin gas in the presence of light capable of promoting chemical action, the supply of chlorin being sufficient to convert the tetrachlorethane into the higher chlorinated ethane desired to be made.

In testimony that we claim the foregoing as our invention, we have signed our names in presence of two subscribing witnesses.

HERMANN HABERLAND.
WALTER SCHAEFER.

Witnesses:

RUDOLPH FRICKE,
AUGUST BRÄGER.