

UNITED STATES PATENT OFFICE.

HERBERT H. DOW AND ARTHUR E. SCHAEFER, OF MIDLAND, MICHIGAN, ASSIGNORS
TO THE DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF
MICHIGAN.

METHOD OF MAKING FERRIC CHLORID.

1,054,400.

Specification of Letters Patent.

Patented Feb. 25, 1913.

No Drawing.

Application filed June 8, 1910. Serial No. 565,751.

To all whom it may concern:

Be it known that we, HERBERT H. DOW and ARTHUR E. SCHAEFER, citizens of the United States, and residents of Midland, county of Midland, and State of Michigan, have jointly invented a new and useful Improvement in Methods of Making Ferric Chlorid, of which the following is a specification, the principle of the invention being herein explained and the best mode in which we have contemplated applying that principle, so as to distinguish it from other inventions.

By the customary method of making ferric chlorid, iron is first dissolved in hydrochloric acid to make the ferrous salt. To this solution is then added a mixture of hydrochloric acid and nitric acids, the former in sufficient amount to furnish chlorin to convert the ferrous to ferric and the nitric acid in smaller amount as an oxidizing agent. The resulting solution of ferric chlorid and nitric acid must then be boiled to drive off the nitric fumes.

By the improvements constituting the present invention, we propose similarly to utilize ferrous chlorid as the basis from which to proceed, the object of such invention being to provide a method of thus making ferric chlorid, whereby but little hydrochloric acid will need be employed, so that a pure article may be used and any contamination by sulfuric or arsenic compounds thereby avoided and at a decreased cost.

A further object is the provision of a method for the carrying on of which only a relatively simple apparatus will be required, while at the same time a high concentration of the product is secured, even where the ferrous chlorid utilized is available only in the form of a relatively weak solution.

To the accomplishment of these and related ends, said invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims.

The following description sets forth in detail one approved method of carrying out the invention, such disclosed mode, however, constituting but one of the various ways in which the principle of the invention may be used.

The weak ferrous chlorid solution which,

as has been explained, is contemplated as forming the starting point in the present process, may contain a small percentage of ferric chlorid. This we preliminarily reduce to the ferrous condition by the addition of a little finely divided iron, as, for instance, fine cast-iron borings or filings. The solution is then boiled down to a specific gravity of 42 Bé., which is readily accomplished in an iron tank with iron coils through which steam is passed. The concentrated solution thus obtained, is then acidified with about one per cent. (1%) by volume of concentrated hydrochloric acid, and is then chlorinated with chlorin gas. The object of adding hydrochloric acid is to prevent the formation of insoluble basic chlorids when commercial chlorin, which contains air as an impurity, is used in the chlorination step. By drying the chlorin before bringing it into contact with the solution, it is possible to obtain a product having a specific gravity of 46 Bé., which may be later reduced to form the U. S. P. solution having a specific gravity of 1.315, or it may be sold in the concentrated form.

In case it is desired to employ the chlorin gas without drying, a corresponding degree of concentration in the resultant product may, nevertheless, be obtained by boiling down the ferrous solution further than the specific gravity (42 Bé.) previously referred to, which is saturation at ordinary room temperature, so that some ferrous chlorid will crystallize out. The crystals thus obtained may then be added to the partly chlorinated solution in the next step, in order to obtain a ferric chlorid solution of high strength. This method of increasing the strength of the ferric solution obtained, may, of course, be employed even when the dried chlorin gas is used, if a ferric solution of exceptionally high strength is desired.

The chlorination step may be carried out in a small way by bubbling the chlorin gas through a series of carboys containing the ferric solution, and in a large way by allowing such solution to flow down through a reaction tower of familiar construction, the chlorin being simultaneously passed through such tower in the opposite direction. Such tower will be filled with coke or other

suitable material, and if the liquor be not sufficiently chlorinated by one passage it may be pumped over the tower again and again as many times as is necessary in order to fully saturate it.

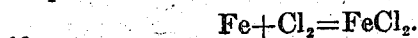
5 As considerable heat is generated by the reaction and the temperature of the liquid thereby correspondingly raised, we find that in practice very little, if any chlorin gas remains in solution in the final product.

10 Instead of evaporating the solution, as hereinbefore described, the desired degree of concentration may be secured by bringing such solution alternately into contact with chlorin in the chlorinator and metallic iron in the saturator, or the solution may be brought into contact with both iron and chlorin in the same apparatus. In this manner the ferrous chlorid is constantly being converted by absorption of chlorin into the ferric salt. This ferric salt is also being constantly reduced to the ferrous by contact with the iron which it dissolves. The reactions are as follows—



The result of the action so far described is that the weak ferrous chlorid solution becomes constantly stronger and stronger by absorption of chlorin and iron, the water remaining substantially the same. The solution would contain at all times under practical conditions both ferrous and ferric chlorid, but chiefly ferrous chlorid. After having been brought in this manner to the proper strength, which would be the equivalent of the strength obtained by evaporation as per the method already described in the specification, the solution can be transferred to a second chlorinating apparatus or otherwise removed from contact with iron. The chlorination would then be continued until all the ferrous salt was oxidized to ferric, when the solution would be drawn off and treated as already described.

45 Instead of starting in the first place with the ferrous chlorid solution, we can start with only iron, water and chlorin. The water would be circulated continuously over a chlorin saturating tower where it would take up chlorin gas. It would then run through a tank or other vessel containing iron in convenient form, as, for instance, scrap iron and preferably wrought iron or steel, where the chlorin would attack the iron and make ferrous chlorid as per the following reaction—



This ferrous solution constantly circulated through a chlorinator and iron saturator would take up chlorin in the chlorinator and iron in the saturator in the manner already described, so that the charge of

water would shortly after starting become a solution of ferrous chlorid the equivalent of that already described.

The foregoing improved process of manufacturing ferric chlorid is also well adapted to the utilization of the by-product from the manufacture of chloroform under the process known as the "Smith" process and described in U. S. Patent No. 753,325 to Albert W. Smith, dated March 1, 1904. In such process, carbon tetrachlorid (CCl_4) is acted upon by iron in the presence of water, with the formation of chloroform as the principal product and ferrous chlorid as a by-product. Upon the chloroform being distilled off from the vessel in which the reaction is accomplished, there remains a mass of hydrated oxid of iron, wet with a solution of ferrous chlorid. While the latter may be recovered in a number of ways, a simple method is to flush out the reaction vessel with water into a settling tank and then allowing the solid matter to subside, whereupon a clear solution may be drawn off. However, if preferred, the mass in the reaction vessel may be pumped out, a small quantity of water being admixed, if necessary, and then passed through a filter press. The ferrous chlorid thus recovered is thereupon treated in the manner already set forth.

Whatever the source of the ferrous chlorid, the advantages of our process are numerous. Evaporation of the corrosive ferric solution is wholly avoided; the boiling of the ferrous solution being a relatively simple matter. The use of nitric acid is entirely avoided and only enough hydrochloric acid is employed to prevent the formation of basic chlorids and to give acidity to the U. S. P. product, as required. In the case of ferric chlorid made by the prevailing acid process, sulfur and arsenic compounds will remain from the acid, unless the latter be free from these elements, and owing to the larger quantity of acid required, the expense of the process is increased if chemically pure acids are used, as they should be, for the compounds referred to are considered detrimental. A further objection to such prevailing process avoided by the present one, is the difficulty of boiling off all the nitric acid, the presence of the latter in the final process being likewise objectionable. None of this latter acid whatever is required in the present process, and since but little hydrochloric acid is employed, a pure article may be used and the contamination of the ferric chlorid, resulting from the introduction of sulfuric or arsenic compounds through such acid, thus avoided. Any free chlorin remaining in the chlorinated liquor may be readily removed by bubbling air through it or by allowing the liquor to flow downward

through a suitable tower against an upward current of air.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the process herein disclosed, provided the step or steps stated by any one of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. The method of making ferric chlorid, which consists in chlorinating a solution of ferrous chlorid containing solid ferrous chlorid.

2. The method of making ferric chlorid,

which consists in acidifying a solution of ferrous chlorid containing solid ferrous chlorid, and then treating such solution with chlorin gas.

3. The method of making ferric chlorid, which consists in acidifying with hydrochloric acid a solution of ferrous chlorid containing solid ferrous chlorid, and then treating such solution with chlorin gas.

Signed by us this 3rd day of June, 1910.

HERBERT H. DOW.

ARTHUR E. SCHAEFER.

Attested by—

MILDRED DAY,

MABEL F. ANDERSON.