UNITED STATES PATENT OFFICE.

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METHOD OF MAKING FORMIC ACID.

960,927. Specification of Letters Patent. Patented June 7, 1910.

No Drawing. Application filed June 23, 1908. Serial No. 440,024.

To all whom it may concern:

Be it known that I, HENRY HOWARD, a citizen of the United States, residing at Boston, in the county of Suffolk and State of Massachusetts, have invented certain new and useful Improvements in Methods of Making Formic Acid, of which the following is a specification.

The object of this invention is to provide an efficient and economical method of producing formic acid from formates.

In U. S. Letters Patent, No. 806,660, granted December 5, 1905 to Max Hamel for a process of making concentrated formic acid it is stated:—"On account of the ease with which formic acid decomposes in the presence of concentrated sulfuric acid the transformation of the dry formates could only be effected with sulfuric acid having a strength of at most 60° Baumé." It is further stated therein:—"The mixing of the dry formate with the sulfuric acid cannot for various reasons be effected so exactly as to obtain a good yield. Thus if high-concentrated sulfuric acid is allowed to drop on formate a very considerable rise of temperature locally occurs which cannot be removed by cooling, as in the mass lumps or the like are formed, so that the mass becomes thick and cannot be stirred, and the sulfuric acid being not rapidly combined, comes in contact with the formic acid set free and decomposes the same." I have discovered that although these statements are correct as applied to a method wherein highly concentrated sulfuric acid is added to commercial sodium formate, they are not applicable to a method wherein the formate is added to a bath of sulfuric acid. In case sulfuric acid of high concentration be added to sodium formate or dropped thereon, particularly if the formate contains such considerable proportions of water as are usually found in the commercial salt, an intense local heating occurs and this appears to initiate a reaction which proceeds rapidly. If however the formate be added to a bath of sulfuric acid the temperature is very readily controlled by the provision of suitable cooling means. It is probable that the observed differences in result between adding sulfuric acid to the formate and adding formate to the sulfuric acid may be wholly or partially accounted for as follows: When sulfuric acid is added to sodium formate, particularly such as contains an appreciable percentage of moisture, a local rise of temperature occurs at the region of contact and a considerable quantity of formic acid is there produced; this acid being an excellent solvent for sodium formate and being by the consistence of the mass prevented from rapidly diffusing therethrough provides conditions under which the reaction proceeds with great rapidity, the development of heat being so rapid that the temperature cannot be effectively controlled. When however the formate is added to a bath of sulfuric acid, even though the latter be of quite high concentration, the bath being suitably agitated, such formic acid as is produced is immediately distributed throughout the mass and does not under these conditions exert so rapid solvent action upon the formate; inasmuch as the formate is slowly or difficultly soluble in strong sulfuric acid the conditions do not lead to the rapid progress of the reaction or to a rapid development of heat. Furthermore, by reason of the excellent heat-conducting properties and high specific heat of sulfuric acid, as well as owing to the fluidity of the bath, the heat is quickly diffused throughout the mass and only a relatively slight rise of temperature is observed: Under these conditions any of the usual cooling means are effective to maintain a constant temperature below that at which substantial decomposition of formic acid occurs.

Formic acid, when mixed in relatively small proportions with strong sulfuric acid, is very slowly decomposed even at normal temperatures, the decomposition being more rapid as the temperature rises; but the decomposition at any given temperature becomes progressively less as the proportion of formic acid increases owing to the progressive dilution of the residual sulfuric acid. In order to proceed with the minimum loss of formic acid by decomposition, it is therefore important that the temperature should be kept as low as practicable during the initial stages of the reaction; and it is preferred to maintain throughout the mass, during the initial stages of the decomposition, a temperature not exceeding 50° C.

The process may be carried into effect by providing a jacketed mixing vessel adapted to withstand sulfuric acid, supplying sulfuric acid of the desired concentration, and slowly

adding to the bath the theoretically requisite quantity of sodium formate, the mixture being cooled as required. Thereafter the temperature may be raised by admitting steam to the jacket, and the formic acid is distilled over, reduced pressure being used if preferred. It has been found that by proceeding in this manner sulfuric acid containing up to 88 per cent. of H_2SO_4 may be employed and a substantially theoretical yield of formic acid obtained. The described method of procedure is highly efficient even with acid of higher concentration.

I claim:—

1. In a method of making formic acid, the step which consists in introducing a formate into a bath of sulfuric acid while maintaining throughout the mass a temperature below that at which substantial decomposition of formic acid occurs.

2. The method of making formic acid which consists in introducing a formate into a bath of sulfuric acid while maintaining throughout the mass a temperature below that at which substantial decomposition of formic acid occurs, and then heating the mass to distil formic acid.

3. In a method of making formic acid, the step which consists in introducing a formate into a bath of sulfuric acid, agitating the mixture, and cooling the same to maintain therein a temperature below that at which substantial decomposition of formic acid occurs.

4. The method of making formic acid which consists in introducing a formate into a bath of sulfuric acid, agitating the mixture, cooling the same to maintain therein a temperature below that at which substantial decomposition of formic acid occurs, and then heating the mass to distil formic acid.

5. The method of making formic acid which consists in introducing a formate into a bath of sulfuric acid while maintaining throughout the mass a temperature below that at which substantial decomposition of formic acid occurs, and distilling formic acid under reduced pressure.

6. The method of making formic acid which consists in introducing a formate into a bath of sulfuric acid, agitating the mixture, cooling the same to maintain therein a temperature below that at which substantial decomposition of formic acid occurs, and distilling formic acid therefrom under reduced pressure.

In testimony whereof, I affix my signature in presence of two witnesses.

HENRY HOWARD.

Witnesses:
IDA MAY GRAHAM,
WILLIAM FRANKLIN OBURG.