UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING FORMATES.

No. 820,374. Specification of Letters Patent. Patented May 8, 1906.

Original application filed April 1, 1904, Serial No. 202,661. Divided and this application filed March 15, 1905. Serial No. 250,698.

To all whom it may concern:

Be it known that we, JULIUS WEISE, FRIEDRICH RIECHE, and ADOLF BARTH, subjects of the German Emperor, and residents of Oestrich-on-the-Rhine, Germany, have invented certain new and useful Improvements in the Manufacture of Formates, of which the following is a specification.

In our application for a United States Patent of April 1, 1904, Serial No. 202,661, we have described a process of manufacturing formates from carbon monoxid and caustic alkali. In a divisional application formed of the original specification of the above application and filed at the same time as the present second divisional application we have described a similar process in which the alkalies of the first process are replaced by alkaline earths. As stated in these two applications, the process requires a sufficient quantity of water, a temperature above 100° centigrade, and a most intimate mixing of the agents for procuring and expediting the reaction. Our further experiments have shown that under these circumstances the carbon monoxid can also act upon carbonates of alkalies in the manner that formates of alkalies are produced and carbonic acid is expelled. The great affinity of carbon monoxid to superheated water, which we have first discovered, causes the intermediary formation of free formic acid, which is capable of expelling weaker acids from compounds of alkalies and of combining with the alkali thus freed. Already in 1856 Berthelot (see *annales de Chimie et de Physique*, Series 3, volume 46, page 480) has shown, it is true, that carbon monoxid reacts upon moist alkali carbonates; but he used a cucurbit of glass and a temperature of 220° centigrade, which proves that he used only so much water for moistening his composition as was required for insuring the reaction ($K_2CO_3 + 2CO + H_2O = 2HCOOK + CO_2$) and entering the molecule of the formate, as otherwise he might have expected an overpressure of twenty and more atmospheres, which of course the glass cucurbit would not withstand. Thus it is evident that he did not employ an aqueous solution and also did not heat the same beyond the boiling-point. The best proof for this assertion is the result attained by him. He only succeeded in changing a few per cent. of his carbonate within from ten to fifteen hours.

Our invention relates to a process similar to those described in the above said two applications, in which the alkalies and the alkaline earths and salts of alkalies, respectively, are replaced by carbonates of alkalies.

Our process consists in making an aqueous solution of the alkali carbonate, heating the solution beyond the boiling-point in a closed vessel, admitting carbon monoxid, and causing the two agents to act upon each other while under agitation or in a finely-divided state.

The rapidity of the reaction increases proportionally to the temperature, while the concentration exercises no great influence if sufficient water be present. The operation must be carried out in closed vessels to prevent the water from evaporating. The closed vessels may be of any known and approved construction. The heating of these closed vessels may be effected in any known manner. In order that the operation may take place rapidly, it is further necessary that the liquid and gas should be in intimate contact, for which purpose any suitable known device can be used. For instance, the liquid may be atomized by stirring devices or nozzles, or it may be distributed in thin layers, and the gas may be blown into the vessel in a finely-divided state.

The new improved process may be carried out in various manners. For attaining the result it is important and necessary that the water be present in a sufficient quantity, that the temperature be maintained above 100° centigrade, and that the agents (a gas and a liquid) be most finely divided and intimately mixed.

If instead of pure carbon monoxid, a mixture of the latter with other gases may be used, these latter gases are blown off during the operation through a suitable valve.

The operation proceeds more slowly with the carbonates of alkalies than in the process described in the above said first application, unless the temperature be correspondingly raised, to which there is no objection, for no decomposition takes place even at 250° centigrade when water is used as herein described.

In opposition to the above-mentioned result attained by Berthelot our process will easily change the whole quantity into a formate within from two to three hours.

Below we give a few examples for carrying out the process.

Example I: A solution of sodium carbonate of 30° Baumé is allowed to trickle on coke in a closed vessel at a temperature of 220° centigrade, and heated carbon monoxid is supplied thereto for about two hours. The intermediate product which forms—namely, formic acid—displaces the carbon dioxid from the carbonate, which carbon dioxid is allowed to escape from time to time by lifting a valve.

Example II: A solution of sodium carbonate of 40° Baumé is most intimately mixed with carbon monoxid in a closed vessel provided with an agitator at a temperature of preferably above 200° centigrade. The formed carbon dioxid is allowed to escape from time to time. After about two hours the theoretical output of sodium formate will be obtained.

What we claim as our invention, and desire to secure by Letters Patent, is—

1. The herein-described process of manufacturing formates, which consists in making an aqueous solution of an alkali carbonate, heating the aqueous solution to a high temperature in a closed vessel, admitting thereto carbon monoxid, and by agitation causing the two agents to act upon each other.

2. The herein-described process of manufacturing formates, which consists in making an aqueous solution of an alkali carbonate, heating the aqueous solution to a temperature above the boiling-point in a closed vessel, admitting thereto carbon monoxid, and by agitation causing the two agents to act upon each other.

3. The herein-described process of manufacturing formates, which consists in making an aqueous solution of sodium carbonate, heating the solution to a high temperature in a closed vessel, admitting thereto carbon monoxid, and by agitation causing the two agents to act upon each other.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

JULIUS WEISE.
FRIEDRICH RIECHE.
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Witnesses:
FRANZ HASSLACHER,
ERWIN DIPPEL,