# UNITED STATES PATENT OFFICE.

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## PROCESS OF MAKING FORMATES.

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*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 Production of Formates, of which the following is a specification.

Our invention relates to improvements in hitherto-known methods of manufacturing formates from carbon monoxid and caustic alkalies, whereby the process is expedited in an extraordinary manner and rendered practical, valuable, and useful, while it yields a good output, which hitherto has never been attained.

Before proceeding to describe our invention we may first state a few facts in order to show the value and importance of our invention.

The synthesis of formates from carbon monoxid and caustic alkalies has been investigated by Berthelot, (see *Annales de Chemie et de Phsique*, Série 3, Vol. 46, 1856, page 480, and Série 3, Vol. 61, 1861, page 463,) by Merz and Tibirica (see *Berichte der Deutschen Chemischen Gesellschaft*, XIII, page 23) and by Goldschmidt. Berthelot first stated that he had obtained but a few per cent. of formate from merely moistened solid caustic alkali at a temperature of 100° centigrade after seventy hours and at a temperature of 220° centigrade after ten hours. When operating with an aqueous solution at the ordinary temperature, he was able to ascertain an insignificant absorption within four months. Later on Berthelot stated that he had made other experiments while employing a "rather remarkable" quantity of water of ordinary temperature and that he succeeded in absorbing a small quantity of carbon monoxid within six weeks while using a large excess of alkali. When employing water of 100° centigrade, he obtained the same insignificant result after from eighty to one hundred hours. From his statements that he used alkalies in the solid state, that he used first "merely moistened" alkalies, afterward a "rather remarkable quantity of water" in opposition to an "aqueous solution" it is quite evident that the "rather remarkable quantity of water" did not mean at all a solution of alkali. Be it as it may, Berthelot was no doubt the first who recognized the importance of the water for the reaction and laid stress on the same. However, Berthelot did not go further, and he did not even succeed in so conducting his experiments as to obtain a result of practical importance, so that his result presented but a theoretical interest. Moreover, it was he himself who at the conclusion of his essay pronounced his synthesis of formates to be a typical example of a slow reaction, and he therefore recommended to synthesize the formate from oxalic acid and glycerin after a known method. Merz and Tibirica equally found the method of Berthelot to be unfit for a profitable manufacture of the formate, and they attempted to improve upon this method. However, they went in the wrong direction, as they employed the alkali exclusively in its solid state—that is, without the use of water—and at the most they moistened the gas—*i. e.*, the carbon monoxid—a little. Goldschmidt went further and showed that the moist gas did not yield a larger output than dry gas.

We have found that Berthelot had made a step in the right direction, for water is very essential for procuring the reaction. However, according to our experiments it will not do to merely moisten the alkali or even to employ a rather remarkable quantity of water. It is absolutely necessary to employ such a large quantity of water as to form solutions of alkalies, so that alkalies in their solid state are no longer used. Ten per cent. of water should be at least employed, and it is preferable to employ considerably more water. At the same time we have found that this quantity of water alone will not do for attaining the result aimed at. According to our experiments it is absolutely necessary to employ the proper temperature, which is essentially higher than 100° centigrade.

The carbon monoxid has the extraordinary property of dissolving in water at an increasing rate as the temperature increases (*vide* the essay of Gerh. Just in *Zeitschrift für physikalische Chemie*, Vol. 37, page 342.) Therefore it is evidently best to exceed the boiling-point of the solution in use, the more so since with a solution of alkali no decomposition of the formed formate under the action of the higher temperature need be apprehended, as hitherto in the hitherto-known methods. Of course care should be taken to prevent the water from evaporating during

the reaction. In other words, the solution should be boiled within a closed vessel, the minimum pressure in the vessel being in accordance with the degree of concentration of the lye and the temperature. We have further found that a third condition must be fulfilled—viz., to bring the two agents into intimate contact with each other. Now that the two agents are a gas and a liquid it is of course evident that the desired intimate mixture can be easily effected with the aid of known technical means, such as stirring devices, nozzles, enlarged contact-faces, &c.

Our invention consists of a process presenting the three features named above, whereby it is rendered valuable, practical, and useful. It may be that the three features have severally been partly described or made public, yet the combination of the three features is novel, and our improved process produces an unexpected and surprising result—viz., the reaction, which by Berthelot was pronounced to be a "typically slow reaction," is now extraordinarily expedited and rendered smooth, and the output is so large that it has never been anticipated heretofore.

Our process consists in making an aqueous solution of a caustic alkali, heating the solution to a high temperature in a closed vessel, preferably beyond the boiling-point of the solution, and in admitting carbon monoxid and causing the two agents to act upon each other while under agitation or in a finely-divided condition. The alkali in this case may be assumed to be caustic soda, while other alkalies and agents will be treated in other patent applications about to be filed.

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, as already stated above. 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 method may be carried out in various manners. Below we give two examples.

Example I: Soda-lye at 40° Baumé is allowed to trickle onto coke in a closed vessel at a temperature of 200° centigrade, and carbon monoxid (which preferably has been previously heated in any known manner) is pumped into the vessel from below in a direction opposite to that of the trickling lye. The carbon monoxid is so rapidly absorbed by the lye that one might think it to be carbonic acid. When properly carrying out the process, the soda-lye leaving the vessel or tower will be found to have been turned into a solution of formate. The latter may be used without any further treatment or be converted into solid formate.

Example II: Soda-lye at 15° Baumé is passed through a horizontal vessel at a temperature of 185° centigrade and therein atomized by means of an agitator, while the heated carbon monoxid is forced into the vessel in a direction opposite to that of the lye. Then the same brilliant result is obtained as before. 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 convenient valve.

The process according to our invention presents the following advantages over those hitherto known: The reaction occurs most rapidly, and as no decomposition can take place the yield is practically that indicated by theory. While in a previous process it was essential in order to exclude water to deprive the bases of water to grind them and mix them with large amounts of an inert substance, these lengthy and costly manipulations are done away with. The troublesome heating of large quantities of dry powder, which conducts heat badly and presents great difficulties in heating, is replaced by the much easier heating of a liquid. Overheating and decomposition of the formate already formed is prevented. The final product need not, as in the previous processes, be lixiviated and does not contain an additional inert substance.

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, 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, 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.

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.