

# UNITED STATES PATENT OFFICE.

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## PROCESS OF MAKING OXALATES.

SPECIFICATION forming part of Letters Patent No. 659,783, dated October 16, 1900.

Application filed December 24, 1897. Serial No. 663,404. (No specimens.)

To all whom it may concern:

Be it known that I, MARTIN GOLDSCHMIDT, a subject of the German Emperor, and a resident of No. 1 Carmerstrasse, Charlottenburg, near Berlin, Germany, have invented certain new and useful Improvements in and Relating to the Production of Oxalates; and I 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.

This invention has relation to the production of oxalates from formates; and it consists in a novel process of producing the oxalates.

The production of oxalates on a commercial scale has heretofore been effected by reacting upon wood-shavings or sawdust with melted potash, (*Lehrbuch der Organ. Chemie von V. Meyer und P. Jacobson*, Vol. I, p. 646.)

After I had discovered a very simple process, well adapted to technical purposes, for producing formates, which consists, essentially, in reacting with carbon monoxide (CO) upon a caustic alkali or alkaline earth under pressure in presence of heat, it became necessary to examine into the proposition of Merz & Weith to utilize the formates in the technical production of oxalates and their experiments in this line, as published in the *Berichte der Chemische Gesellschaft—i. e.*, reports of the German Chemical Society, Vol. 13, p. 721—and as I shall have occasion to repeatedly refer to these reports I will hereinafter do so by volume and page only.

Merz & Weith have established by a series of experiments that it is possible to convert a formate into an oxalate by simply heating the formate to 440° centigrade, (Vol. 15, p. 1509.) The proportion of oxalate obtained is in many cases considerable, but in no case does it correspond with the theoretical yield. In the most successful of the numerous experiments made by them they obtained seventy-one per cent. of the theoretical yield, (Vol. 15, p. 1510, experiment No. 15 in the tabulated statement.) In order, however, to arrive at a yield that is in any manner satisfactory, these discoverers state in volume 13, page 720, that a brusque heating or, as stated in volume 15, page 1508, a fierce or violent or stormy heating, or, as stated in volume 15, page 1510, a rapid heating is absolutely

necessary, because, as they state in volume 15, page 1509, formate of soda, for instance, will be chiefly converted into a carbonate at a temperature of 360° centigrade, while at a temperature of 440° centigrade it will be chiefly converted into an oxalate. It follows naturally that the heating of the formate from 360° to 440° centigrade must be effected rapidly to avoid the undesirable formation of a carbonate. In their experiments Merz & Weith used relatively very small quantities of formate, in one case two grams, (Vol. 13, p. 720,) and, in fact, in their other experiments, as clearly shown by their description and drawings, (Vol. 15, p. 1508,) they used only insignificant quantities. In the use of such small quantities of formate there are no great difficulties in heating the same brusquely, fiercely, or stormily and rapidly, as they say; but they acknowledge that they are doubtful as to whether a large quantity of formate, such as would be required to make the process a commercial success, could be heated in the manner they describe. These doubts are repeatedly expressed, (Vol. 15, p. 1513;) but they finally content themselves with the consoling information that the solution of the problem from a technical standpoint does not seem impossible, (Vol. 15, p. 1513.) In fact, however, before my invention an apparatus had not been constructed in which a large quantity of formate—as, for instance, one hundred kilos—could be heated as described by Merz & Weith to 440° centigrade without subjecting the material gradually to every degree of heat from a normal up to 440° centigrade. In this case there is not the slightest doubt that the ominous or critical temperature of 360° centigrade is gradually reached and that this temperature must gradually rise, so that the effects of this critical temperature will undoubtedly assert themselves.

I have made all of the experiments of Merz & Weith and found them in every respect correct; but I never succeeded even with so small an amount of formate as a few hundred grams in producing by heat a sufficient quantity of oxalate to warrant the belief that their process is commercially available. This I attribute (irrespective of peculiar phenomena due to the fact that formates are poor



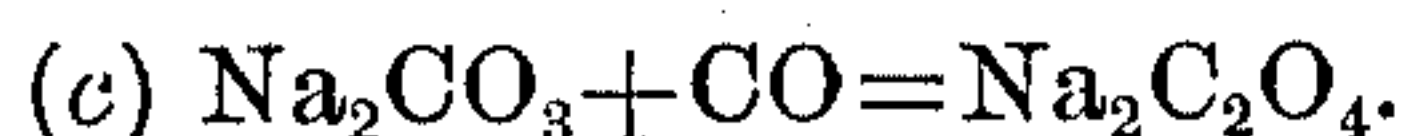
conductors of heat, which results in partial superheating) principally to the circumstance that it is impossible to brusquely, fiercely, or stormily and very rapidly heat even one hundred grams of formate to 440° centigrade. Experiments made by me in a different direction resulted in the following observations: that if, for instance, formate of soda is chiefly converted into a carbonate at a temperature of 360° centigrade and chiefly into an oxalate at a temperature of 440° centigrade the reaction at a temperature of 360° must take place in accordance with the following equation:



At 440° the reaction should take place in accordance with the equation found in all chemical text-books, to wit:



It seemed to me, however, that the conversion proceeded differently, especially in view of the hitherto generally-accepted theory that decomposition takes place more energetically at lower than at higher temperatures. At a lower temperature it is said the formate should give up carbon monoxide and hydrogen, but hydrogen only at a higher temperature. I thought that I would be justified in assuming that the reaction proceeded under all circumstances in accordance with equation "a" and that the oxalate is formed by a secondary process, during which the carbon monoxide combines *in statu nascendi* with the soda already formed according to the following equation:



I believed this assumption the more justifiable because the extraordinary chemical affinity of carbon monoxide was well known. These experiments of mine have verified the correctness of my assumption that the carbon monoxide will first combine with the previously-formed soda, and this fully agrees with the fact that in all of the experiments made by Merz & Weith there is not a single one in which a material proportion of alkali carbonate was not formed. The generally-popular equation (b) does not offer an explanation of this fact. With this supposition as a basis I soon concluded that it would not be impossible to increase the yield of oxalate by avoiding the formation of a carbonate when heating the formate, and I found that this could be readily effected by addition to the formate of a carbonate with which the carbon monoxide could combine in lieu of combining only with the carbonate formed by the heating of the formate and that this combination would take place the moment the formate commenced to give up carbon monoxide, which in the absence of a carbonate could not take place until a certain quantity of carbon monoxide had escaped and sufficient soda had been formed to bind the carbon monox-

ide. Experiments have conclusively shown by the extraordinary and surprising results obtained that my theory was correct, in that a mixture of soda and sodium formate without resorting to brusque, stormy, or fierce or rapid heating yielded oxalate in large quantities even at a lower temperature than 440° centigrade, the reaction being in fact complete at 360° centigrade. However remarkable these results seemed to be their explanation is very simple. Formate is decomposed when heated to 360° centigrade into carbon monoxide and carbonate. The nascent carbon monoxide has a great affinity for carbonates, or, in other words, is readily absorbed thereby. This affinity between the two chemicals is at a temperature of 440° centigrade especially great, but is also present at a temperature of 360°, of course to a less extent; but if the absorbing properties of one substance are greater than those of another it is only necessary in order to insure complete absorption to increase the quantity of the less absorbent substance. It is therefore necessary at a temperature of 360° centigrade to add a greater quantity of soda to the formate in order to insure the complete absorption of the carbon monoxide than would be necessary at a temperature of 440° centigrade and, contrariwise, Merz & Weith were compelled by reason of the absence of sufficient soda to endeavor to heat the formate as quickly as possible to 440° centigrade in order to avoid the escape into the atmosphere of the carbonic oxid evolved at lower temperatures. By the addition of soda the brusque, fierce, or stormy or very rapid heating to 440° centigrade of the formate becomes unnecessary, hence affords a convenient means whereby oxalates can be produced from formates on a commercial scale.

In carrying out my invention I simply mix the soda intimately with the formate in the proportion of about four parts of sodium formate with about five parts of soda, which proportions have proven very practical. The mixture is then heated in a suitable vessel, as an iron vessel, in a lead-bath, while being stirred to facilitate a uniform heating, to from 400° to 410° centigrade, and preferably under exclusion of atmospheric air, and provision of means to collect the hydrogen gas evolved for use as a means of observing the procedure of the reactions, said gas being caused to flow through water. The formation of oxalate proceeds with tolerable rapidity and is completed in about from thirty-five to forty minutes. The evolution of hydrogen is at times very lively, and as soon as this evolution ceases the reaction is completed. The product of the reactions contains oxalate and carbonate, which owing to the great difference in their solubility can very readily be separated. I preferably use for this purpose water heated to about 33° centigrade, because it then has its greatest solvent power for soda, and use about twice as much water as



there is soda in the mixture. The soda solution so obtained is absolutely colorless. There is not a trace of coloring-matter or a slimy substance present, as is the case in the production of oxalates from sawdust, and from this solution the soda is readily obtained by evaporation and can again be used in the process. The remaining oxalate of soda, which is also entirely white, can then be worked up into oxalic acid or oxalates in the well-known manner by means of lime milk. The described manufacture of oxalic acid can be combined in a most simple manner with the process for the manufacture of formates described in my German Patent No. 86,419. It is therefore possible to give to the carbon monoxide a quasi solid form, either as a formate or oxalate.

The differences between the process which forms the subject-matter of my invention and the process described by Merz & Weith herein referred to are the following: first, increase in the yield of oxalates relatively to the theoretical yield; second, the avoidance of a brusque, fierce, or stormy or rapid heating, which for technical purposes cannot be done, except in complex apparatus not yet available; third, the advantage and economy of lower temperatures, and, fourth, the avoidance of overheating, which is liable to occur in

view of the poor heat-conductive power of formate and the disadvantages inherent thereto or resulting therefrom.

Having thus described my invention, what I claim as new therein, and desire to secure by Letters Patent, is—

1. The process, which consists in first mixing a carbonate with a formate and then heating the mixture sufficiently to form monoxide of carbon and hydrogen, whereby the former combines with the carbonate to form the oxalate in a proportion nearly equal to the proportion of formate in the mixture, substantially as set forth.

2. The process which consists in first mixing a formic-acid salt with an alkali carbonate, then heating the mixture sufficiently to form monoxide of carbon and hydrogen, whereby the former combines with the carbonate to form oxalate in a proportion nearly equal to the proportion of formate in the mixture, substantially as set forth.

In testimony that I claim the foregoing as my invention I have signed my name in presence of two subscribing witnesses.

MARTIN GOLDSCHMIDT.

Witnesses:

MAX C. STACHLER,  
CHARLES H. DAY.