

# UNITED STATES PATENT OFFICE.

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## PROCESS OF MAKING SALICYLIC ACID.

SPECIFICATION forming part of Letters Patent No. 529,182, dated November 13, 1894.

Application filed April 25, 1894. Serial No. 508,985. (No specimens.) Patented in Germany February 20, 1893, No. 73,279; in France August 23, 1893, No. 232,352, and in England September 9, 1893, No. 17,002.

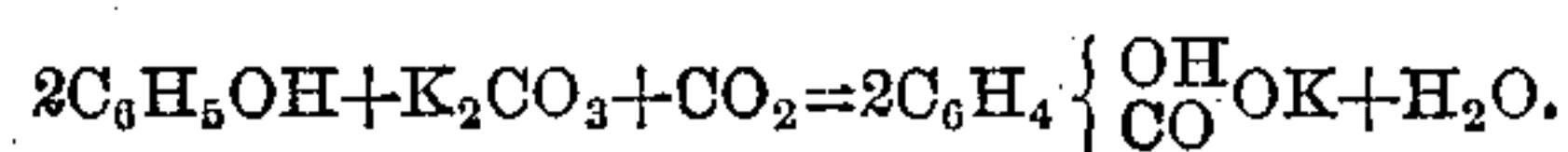
To all whom it may concern:

Be it known that I, SIEGFRIED MARASSE, a subject of the King of Prussia and German Emperor, residing in the city of Berlin, in Prussia, Germany, have invented certain new and useful Improvements in Processes of Making Salicylic Acid, (for which Letters Patent were granted to me in Germany, No. 73,279, dated February 20, 1893; in France, No. 232,352, dated August 23, 1893, and in Great Britain, No. 17,002, dated September 9, 1893,) of which the following is a specification.

In the processes heretofore used for making salicylic acid on a large commercial scale, it is obtained from phenolates of the alkalies or alkaline earths. These phenolates have to be absolutely free of water, which requires a tedious treatment, previous to subjecting them to the action of carbonic acid gas in open or closed vessels at a gradually increasing temperature. On the other hand, according to an experiment published by Drechsel in the *Zeitschrift für Chemie* for the year 1865, page 580, salicylic acid is found to generate "slowly and in small quantities," when a mixture of phenol, potassium bicarbonate ( $\text{KHCO}_3$ ) and water is placed in a glass-tube, which is then sealed by melting and in which said mixture is kept for several days at a temperature of  $160^\circ$  centigrade. Moreover, from experiments made by Senkofer, Brunner and Sarlay, published in the *Wiener Academische Berichte* volume 80, pages 504 to 524, and volume 84, pages 323 and 331, it appears that when phenols containing more than one atom of oxygen are heated for fourteen hours with ammonium carbonate and potassium bicarbonate in an aqueous solution, the mono or dicarboxylic acid of the respective phenol is produced. No such action, however, takes place on the phenol itself,  $\text{C}_6\text{H}_5\text{OH}$ . These investigators emphasize repeatedly the fact that from phenol proper, under the action of ammonium carbonate and water, they always obtained "only traces" of salicylic acid. Consequently, owing to these extremely unsatisfactory results, neither the process described by Drechsel, nor that of Senkofer, Brunner and Sarlay, can be used on a large scale for manufacturing the most important of the aromatic oxy-carbo-acids, known as salicylic acid.

The object of my invention is to furnish a process by which a complete reaction is obtained without the necessity of producing and drying the phenolates; and the invention consists of the process of making salicylic acid by subjecting a dry mixture of phenol with neutral potassium carbonate or potashes in excess to the action of carbonic acid gas at a gradually increased temperature, as will be fully described hereinafter and finally pointed out in the claims.

In carrying out my improved process, phenol is intimately mixed with neutral potassium carbonate, and subjected in a closed receptacle to the action of the required quantity of carbonic acid gas at a gradually increased temperature. The best temperature is between  $130^\circ$  and  $160^\circ$  centigrade. It is especially important that an excess of potassium carbonate be used, so as to prevent the mixture from caking when heated, as thereby the carbonic acid gas would be prevented from entering freely either wholly or in part, into the mixture and acting on the same. As soon as the temperature most advantageous for the reaction is reached, the carbonic acid gas will act readily and instantly, as can be observed on the pressure gage. When, after cooling, the receptacle is opened, it will be found that the phenol has been converted almost completely into potassium salicylate. The reaction, in which apparently no intermediate products are formed, takes place according to the following equation:



By using the carbonates of other alkalies than potassium the production of salicylic acid cannot be obtained in the way described. From the potassium salicylate salicylic acid is obtained in the well-known manner, by first precipitating it by mixing it with a mineral acid, and then purifying it by recrystallization and admixture of animal charcoal.

My improved process differs from the processes heretofore known essentially in the following three points, which clearly establish the novelty of the same:

First. The production of salicylic acid according to my improved process takes place under separation of water, as appears from the



equation representing the reaction. The process even permits some water to be added or to be present in the re-agents without preventing the formation of salicylic acid, provided  
5 always that a sufficient quantity of potash is present to prevent the mixture from caking or solidifying. In the processes hereinbefore described, the presence of water has to be carefully avoided.

10 Second. It was observed and stated by Baumann, (*Berichte der Deutschen Chemischen Gesellschaft*, volume 10, page 686,) that on boiling phenol for fourteen hours with a solution of potash under development of carbonic acid, potassium phenolate will be  
15 formed. It might therefore be presumed that in my before-described process the formation of potassium phenolate would precede the generation of salicylic acid. That this is not the case and that in a closed receptacle, the reaction observed by Baumann does not take place, is proved by the following experiment:  
20 When potassium phenolate is subjected in a closed vessel in the presence of water to the action of a small quantity of carbonic acid, phenol will be set free and potassium carbonate formed. This separation occurs at lower as well as at higher temperatures. In my improved process, in which water is generated, potassium carbonate comes without  
30 the least doubt into simultaneous action with the carbonic acid. The ready formation of salicylic acid is mainly based upon the joint and simultaneous action of the potash and carbonic acid on the dry porous mixture of  
35 the phenol and potash.

Third. A further important feature of my improved process is the intimate mixture of the phenol with potash, the latter being added  
40 in excess to such an extent that the mixture, even at a higher temperature, is retained in the form of a dry powder, so that it can be easily penetrated and attacked in all its parts by the carbonic acid gas. This dry porous  
45 intimate mixture of the ingredients is a preliminary condition for the reaction and the complete conversion of the phenol into sali-

cylic acid. This fact also distinguishes my new process from that of Drechsel, where likewise after heating are present potash, 50 phenol, water and carbonic acid, but independently of each other. The carbonic acid gas, however, is not confronted by a loose porous mixture, but is in the presence of two superposed liquids which do not penetrate 55 each other, the one being an aqueous, the other an oily substance, which prevents them from acting one upon the other. The oily liquid separates the carbonic acid from the aqueous liquid, and though the heating be 60 continued for days, the carbonic acid will only generate a very small amount of salicylic acid. Consequently, no useful result is obtained in this instance, while by my improved process, a very advantageous process 65 is obtained, that can be carried out on a large scale and which yields a high percentage of salicylic acid.

Having thus described my invention, I claim as new and desire to secure by Letters 70 Patent—

1. The process herein-described of making salicylic acid, which consists in subjecting a dry mixture of phenol and potassium carbonate in excess to the action of heat and 75 carbonic acid gas under pressure until the reaction is completed and potassium salicylate obtained, and then producing salicylic acid from the potassium salicylate in the well-known manner, substantially as set forth. 80

2. In the process of making salicylic acid, the step of producing potassium salicylate by subjecting a dry mixture of phenol and potassium carbonate in excess to the action of heat and carbonic acid gas under pressure, 85 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.

SIEGFRIED MARASSE.

Witnesses:

PAUL EBERTY,  
GUISAR ZÉIKER.