UNITED STATES PATENT OFFICE.

EDWIN O. BARSTOW, OF MIDLAND, MICHIGAN, ASSIGNOR TO THE DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF MICHIGAN.

PROCESS OF MANUFACTURING BENZOATE.

939,941. Specification of Letters Patent. Patented Nov. 9, 1909.

No Drawing. Original application filed October 25, 1905, Serial No. 284,402. Divided and this application filed March 14, 1906. Serial No. 305,959.

To all whom it may concern:

Be it known that I, EDWIN O. BARSTOW, a citizen of the United States, resident of Midland, county of Midland, and State of Michigan, have invented a new and useful Improvement in Processes of Manufacturing Benzoates, (Case C,) of which the following is a specification, the principle of the invention being herein explained and the best mode in which I have contemplated applying that principle, so as to distinguish it from other inventions.

My invention relates to processes of making benzoic acid and benzoates and particularly to the manufacture of calcium benzoate.

The particular subject-matter of this invention has been divided out of a pending application for U. S. Letters Patent, filed October 25, 1905, Serial No. 284,402.

Said invention consists of steps hereinafter fully described and specifically set forth in the claims.

The following description sets forth in detail certain steps embodying my invention, such disclosed steps constituting but one of various ways in which the principle of the invention may be used.

Some of the various methods by which benzoic acid and benzoates have heretofore been manufactured are as follows: (1) From gum benzoin and other natural gums by sublimation or extraction, such processes involving the treatment of the gum simply with heat, or with an alkaline solution to dissolve the benzoic acid, and the subsequent precipitation by means of a mineral acid. (2) From urine and hippuric acid by well-known processes. (3) From benzyl chlorid, benzal chlorid or benzo-tri-chlorid, by the following processes: (*a*) From benzyl chlorid by oxidation with hot dilute nitric acid, giving as resultant products benzoic acid and hydrochloric acid. (*b*) From benzal chlorid as a by-product in the manufacture of benz-aldehyde, the benzal chlorid being treated with a solution of lime. (*c*) From benzo-tri-chlorid by heating with water under pressure, with lime and water or a solution of caustic soda and whiting.

My invention relates to those of the above-mentioned methods in which benzoic acid or the benzoates are manufactured from homologues of benzene containing one side chain, and particularly to that method in which calcium benzoate is manufactured from benzyl chlorid, although my improved process may be used in the manufacture of benzoates from benzal chlorid, benyl alcohol or benz-aldehyde.

The particular subject-matter of this invention relates to the formation of products intermediate of such side chain products and benzoates, such as benzyl alcohol and benz-aldehyde, during the process of obtaining benzoates from members of the benzene series of hydrocarbons. When manufactured by the old method noted above from benzyl chlorid, the old process has been subject to the difficulty that the nitric acid is an expensive oxidizer and corrosive so that glass or stoneware apparatus is required and the process as a whole has been found unsuitable for commercial purposes. As manufactured by the old method noted above from benzal chlorid, benzoic acid and the benzoates are obtained as by-products only, which is unsatisfactory when the main purpose sought is the manufacture of benzoic acid or benzoates. When manufactured by the old method noted above from benzo-tri-chlorid, the old process is subject to the difficulty that the resultant product always contains impure acids in the form of chlor-benzoic acids.

In the carrying out of my improved process I produce a chlorin substitution product of one of the homologues of benzene, such product having only one side chain, and then I convert such product into an oxygen containing oxidation product intermediate between said homologue of benzene and a benzoate by any suitable means, such as heating with a solution of sodium carbonate and then I oxidize such intermediate product to benzoic acid or a benzoate by means of a compound containing chlorin. However, I may start with the chlorin substitution product and in that case my improved process would consist of only two steps, viz., the conversion of such chlorin substitution product into an intermediate product and then the oxidation of the latter to a benzoate by means of the chlorin-containing compound. If I should start with the intermediate product, such as benzyl alcohol or benz-aldehyde, my process would then consist of only one step, viz.,

the oxidation of such intermediate product by means of the chlorin-containing compound. In order to typify the methods by which my process may be effected I shall describe the same as carried out when I manufacture that derivative of toluene which has one atom of chlorin in one side chain, viz., benzyl chlorid, convert this into benzyl alcohol and then oxidize the latter to a benzoate by means of bleaching powder and lime. It will be understood, however, that other compounds may be utilized without departing from the spirit of my invention.

When toluene is chlorinated to the first stage, either benzyl chlorid or a chlor-toluene is formed and the tendency is for each molecule of the toluene to take one atom of the chlorin before any molecule takes a second atom, this atom of chlorin going into the side chain or methyl radical of the toluene in a great majority of cases, if the conditions under which the chlorination takes place are proper, such conditions being principally that the chlorination be aided by heat and take place in the sunlight. If the chlorination is effected in the cold and dark, or there be present any carrier such as iodin or ferric chlorid, the chlorin will tend to go into the ring and not into the side chain. This tendency of each molecule to take up an atom of chlorin before any molecule takes up its second atom is probably due to the fact that the toluene is more volatile than either benzyl chlorid or chlor-toluene, so that as the chlorin bubbles up through the liquid under treatment, the toluene vaporizes and thus comes into more intimate contact with the chlorin than does the part still remaining as a liquid. When the chlorin atom that is taken up goes into the side chain, it forms benzyl chlorid, and when it goes into the ring, as it does in a comparatively few cases, it forms a chlor-toluene. This chlor-toluene will not form a benzoic acid when treated according to my process, so that it will not form an impurity in my resultant product. I therefore obtain a benzoate which holds very little ring chlorin, whatever it does hold being obtained from those few molecules of toluene which took up two atoms of chlorin, of which two atoms one went into the ring and one into the side chain; because, if both of the chlorin atoms or all three of them, if some molecules of toluene had taken up three atoms, had gone into the ring, they would not form a benzoic acid at all, or, if they had gone into the side chain, they would have formed a benzoic acid containing no ring chlorin. It will be understood, therefore, that if I pass into the toluene only such a quantity of chlorin as is necessary to furnish each molecule with one atom, substantially all of such toluene will be chlorinated to the first stage in the manner described above, and by far the greater part of it will be in the form of benzyl chlorid, the remaining smaller part being in the form of chlor toluene, which latter is inert, when I convert the benzyl chlorid into the intermediate product, and then oxidize, as hereinafter fully described, and, consequently, does not form a chlor-benzoic acid which would be an impurity in the resultant product. It will be seen, therefore, that if I should chlorinate the toluene to the second or third stage, the probabilities would be greatly increased of obtaining a product in which chlorin had entered both the ring and the side chain of the toluene, and thus result, when the oxidation is effected, in the production of a chlor-benzoic acid, as noted above.

Another objection to the chlorination of the toluene to the second stage, viz: to benzal chlorid or to the third stage, viz: to benzo-tri-chlorid, is that much more apparatus is required to treat a given amount of toluene in a given time, which is uneconomical since the chlorination of toluene is at the best a delicate and comparatively expensive operation. Furthermore, the rate of absorption of the chlorin is much faster during the first stage of the chlorination than it is during the later stages; also, the loss due to decomposition is not nearly so great when benzyl chlorid is formed as it is when benzo-tri-chlorid is formed, due to the fact that the liquid remains in the apparatus less than one-third as long, and also to the fact that under the conditions benzo-tri-chlorid decomposes more readily than benzyl chlorid.

My improved process then consists in chlorinating toluene to the first stage, viz. to benzyl chlorid, converting the latter to benzyl alcohol by heating with a solution of sodium carbonate or by any other suitable method and then oxidizing the benzyl alcohol to calcium benzoate by heating it with a solution of bleaching powder and lime, calcium benzoate thus being formed, which crystallizes out upon cooling the solution. Sodium benzoate may be obtained by adding a solution of sodium carbonate to a hot solution of calcium benzoate. If the chlorination has reached the second stage, the benzal chlorid thus formed would be converted into benz-aldehyde and then the latter oxidized to calcium benzoate by heating it with a solution of bleaching powder and lime.

As a guide in practically working out my process, the following data, illustrating the relative quantities and course of procedure where the specific materials named are employed, is furnished: One part of the benzyl alcohol, which is oily in character as is well known, is agitated with three parts of water to form an emulsion. Such emulsion is thereupon run into a solution of bleaching

powder, lime, and water prepared by adding four parts of the powder, containing 35% of available chlorin, to twenty-five parts of water and then adding one-tenth part of slaked lime. The entire mixture, after stirring is finally heated in a suitable apparatus, whereupon the following reaction takes place:—

$$2C_6H_5CH_2OH+4CaOCl_2+Ca(OH)_2=Ca(C_6H_5COO)_2+4CaCl_2+4H_2O.$$

The apparatus preferably employed consists of a common cement-lined iron retort provided with a reflux condenser, an agitator, and direct steam and water connections for regulating the temperature. The preferred temperature is about 95° C.

Bleaching powder or chlorid of lime is made by absorbing chlorin in slaked lime and the oxidizing constituent of bleaching powder may be regarded as having the formula $CaOCl_2$. However, the latter may be regarded as a mixture in equal molecular proportions of calcium chlorid and calcium hypochlorite, thus:

$$2CaOCl_2=CaCl_2+Ca(OCl)_2$$

and in this case the calcium hypochlorite would be regarded as the active oxidizing constituent. In oxidizing a derivative of toluene with bleaching powder it is necessary for practical reasons to have lime present in excess in order to neutralize the benzoic acid as soon as formed, thus keeping the solution always alkaline. If the solution is allowed to become acid, the hypochlorite is decomposed with liberation of free chlorin and conversion of such hypochlorite into chlorate and chlorid. Obviously a relatively poor yield of benzoic acid will thus be obtained. Since ordinary bleaching powder always contains a considerable amount of caustic lime, it is possible to effect the oxidation of the benzyl alcohol without the addition of a further quantity of lime, but better results can usually be obtained by the use of an additional quantity of the same.

While I prefer to use chlorid of lime as an oxidizing agent, I use other substances of a similar nature containing hypochlorites, in which the calcium is replaced by some other metal. Such substances may be obtained by absorbing chlorin in alkaline earth hydrates either in solution or in the solid state. Furthermore, hypochlorite-containing substances having similar properties may be obtained by absorbing chlorin in alkaline hydrates either in solution or in the solid state, and in connection with such a method I wish particularly to refer to my pending application for U. S. Letters Patent, Serial No. 305,958, filed March 14, 1906. As an examule of the foregoing, sodium hypochlorite is obtained, which is an active oxidizing agent, when chlorin is absorbed in a solution of sodium hydrate, thus:

$$2NaOH+Cl_2=NaCl+NAOCl+H_2O.$$

I prefer to use lime as the reagent with which to neutralize the acid formed, but it is not necessary to do so, since I can use the hydrate of any alkaline or alkaline earth metal. Furthermore, I prefer to use toluene as the source of benzoic acid, but any of the homologues of benzene containing one side chain will serve the purpose.

The gist of my invention, then, consists in the oxidation to benzoates, by means of bleaching powder or similar hypochlorite-containing substances, of benzyl alcohol, benz-aldehyde or similar side-chain derivatives of the homologues of benzene, such derivatives being oxygen containing oxidation products intermediate of the chlorin derivatives of such homologues and the benzoate being formed. These intermediate products which require oxidation to form benzoic acid are obtained from the chlorin derivatives of members of the benzene series of hydrocarbons in any suitable manner.

It will be noted that while I prefer to stop the chlorination of the toluene at the first stage, viz., at the formation of benzyl chlorid, it is not necessary to do so, but that I can stop at any point short of the complete conversion to benzo-tri-chlorid, such chlorinated toluene then being in the form of a mixture of toluene, benzyl chlorid, benzal chlorid, benzo-tri-chlorid, and small amounts of decomposition products and compounds with chlorin in the ring, this mixture, upon being treated with a solution of bleaching powder and lime, being oxidized directly to calcium benzoate without further chlorination, which further chlorination would give a product yielding a less pure calcium benzoate. In this process I convert the chlorin derivatives of toluene into intermediate products and then oxidize the latter to benzoates, as, for instance, converting benzal chlorid to benz-aldehyde by heating with a solution of lime and then oxidizing the benz-aldehyde to calcium benzoate by heating with a solution of lime and bleaching powder; yet, I might oxidize the chlorin derivatives of toluene directly to calcium benzoate by heating with a solution of lime and bleaching powder, or by heating with a solution of sodium hydrate and sodium hypochlorite, respectively, and, in this connection, I refer to my pending applications for U. S. Letters Patent mentioned hereinbefore, viz., Serial No. 284,402, and filed October 25, 1905 and Serial No. 305,958, filed March 14, 1906.

Benzo-tri-chlorid does not require any oxidation to form benzoic acid and hence my process is not applicable thereto. By my im-

proved process I obtain a substantially pure benzoic acid, due to the small percentage of chlorinated toluene which contains its chlorin both in the side chain and in the ring; furthermore, in order to obtain a given amount of benzoates, I require less than one-third of the apparatus and only one-third of the amount of chlorin gas that has been necessary heretofore when the toluene was converted into benzo-tri-chlorid, the remaining oxidation being effected by means of chlorid of lime which is easily and cheaply made by absorbing chlorin in slaked lime.

Having thus described my invention in detail, that which I particularly point out and distinctly claim is:

1. In a process of manufacturing benzoates, the step which consists in oxidizing to the acid a partially oxidized oxygen-containing product of a member of the benzene series of hydrocarbons by means of a chlorin-containing reagent in the presence of a basic neutralizing reagent and a suitable solvent.

2. In a process of manufacturing benzoates, the step which consists in oxidizing to the acid a partially oxidized oxygen-containing product of a member of the benzene series of hydrocarbons by means of a chlorin-containing reagent in the presence of an alkaline earth hydrate and a suitable solvent.

3. In a process of manufacturing benzoates, the step which consists in oxidizing to the acid a partially oxidized oxygen-containing product of a member of the benzene series of hydrocarbons by means of a chlorin-containing reagent in the presence of lime and water.

4. In a process of manufacturing benzoates, the step which consists in oxidizing to the acid a partially oxidized oxygen-containing product of a member of the benzene series of hydrocarbons by means of bleaching powder in the presence of a suitable solvent, such bleaching powder containing sufficient lime to neutralize the acid formed by the reaction.

5. In a process of manufacturing benzoates, the step which consists in oxidizing to the acid a partially oxidized oxygen-containing product of a member of the benzene series of hydrocarbons by means of bleaching powder in the presence of water and of lime in excess of that contained in said bleaching powder.

6. In a process of manufacturing benzoates, the step which consists in oxidizing benzyl alcohol to the acid by means of a chlorin-containing reagent in the presence of a basic neutralizing reagent and a suitable solvent.

7. In a process of manufacturing benzoates, the step which consists in oxidizing benzyl alcohol to the acid by means of a chlorin-containing reagent in the presence of an alkaline earth hydrate and a suitable solvent.

8. In a process of manufacturing benzoates, the step which consists in oxidizing benzyl alcohol to the acid by means of a chlorin-containing reagent in the presence of lime and water.

9. In a process of manufacturing benzoates, the step which consists in oxidizing benzyl alcohol to the acid by means of bleaching powder in the presence of a suitable solvent, such bleaching powder containing sufficient lime to neutralize the acid formed by the reaction.

10. In a process of manufacturing benzoates, the step which consists in oxidizing benzyl alcohol to the acid by means of bleaching powder in the presence of water and lime in excess of that contained in said bleaching powder.

11. The process of manufacturing benzoates, which consists in forming an emulsion of benzyl alcohol with water, mixing such emulsion with a solution of bleaching powder to which has been added a quantity of slaked lime, and thereupon heating.

Signed by me this tenth day of March, 1906.

EDWIN O. BARSTOW.

Attested by—
WM. L. BAKER,
EDW. A. LANE.