ABSTRACT: In a process for the spray drying of alkali metal phenates the carbon dioxide content of the gases leaving the drying chamber serves as an indication of the alkalinity of the product.
METHOD OF CONTROLLING THE ALKALINITY OF ALKALIMETAL PHENATES

This invention relates to a process for the recovery of alkali metal salts from aqueous solutions thereof. More particularly, it relates to a process for the production of substantially anhydrous alkali metal phenates and carbamates that have uniform low alkalinity.

Alkali metal phenates are used commercially in the production of hydroxyaromatic acids by the Kolbe process. In this process the alkali metal phenates are reacted with carbon dioxide under pressure and in the absence of water to produce salicylic acid, p-hydroxybenzoic acid, and other hydroxyaromatic acids. The alkali metal phenate starting material is generally prepared by the reaction of a phenol with an alkali metal hydroxide in aqueous solution. Various methods have been proposed for the recovery of the alkali metal salts in substantially anhydrous form, but none has given entirely satisfactory results. For example, when an aqueous solution of an alkali metal phenate is dried in pans, the drying must be carried out at relatively low temperatures because rigorous heating causes decomposition and discoloration of the product. The resulting product, which contains small amounts of water, tends to cake and must be ground before it can be used industrially. A process for the spray drying of alkali metal phenate solutions under prescribed conditions is disclosed in copending U.S. Patent application Ser. No. 584,576, which was filed by Dege and Cheremisinoff on Oct. 5, 1966. This process results in the rapid drying of the alkali metal phenate and in the formation of a finely divided product. Because product decomposition during and after drying results when excess phenol is present in the aqueous alkali metal phenate solution, this process is usually carried out using feed solutions that contain about 1 percent to 3 percent excess alkali metal hydroxide. The presence of these amounts of excess alkali has been found to adversely affect the yield when the alkali metal phenate is carbonylated. For example, when the sodium phenate that is carbonylated contains 0.5 percent excess sodium hydroxide a conversion of 85 percent and a yield of 91 percent of salicylic acid are obtained, whereas when 1.0 percent excess sodium hydroxide is present the conversion is 80 percent and the yield is 88 percent, and when 2 percent excess sodium hydroxide is present the conversion is about 70 percent and the yield is about 80 percent.

In the spray drying processes carried out heretofore, the alkali metal phenate feed solutions have been prepared by a process in which the required amounts of a phenol and an aqueous solution of an alkali metal hydroxide are placed in separate weigh tanks and then emptied into a mix tank. After mixing, the alkali metal phenate solution is discharged into the spray dryer feed tank which is large enough to hold about ten of the mix tank batches. The feed solution is analyzed at regular intervals to make certain that it has the required composition. When the proportions of phenol and alkali metal hydroxide in the solution are incorrect as the result of malfunctioning of the weighing system, spillage, the use of recovered phenol containing excessive amounts of impurities, and the like, the necessary adjustments are made in the amounts of phenol or alkali metal solution that are being used in the preparation of the spray dryer feed solution. Because chemical analysis of the feed solution is time consuming and cannot be completed in less than about 2 hours, it is ordinarily carried out no more frequently than once or twice a day. In addition analysis by chemical procedures is reproducible only to within about ± 0.5 molar percent of either alkali metal hydroxide or phenol. To avoid the possibility that an excess of phenol will be present at any time in the feed solution, it is customary to use at least about 0.5 percent excess alkali metal hydroxide in the spray dryer feed solution, and excesses of about 1 percent to 3 percent of alkali metal hydroxide have usually been used.

As has been indicated herebefore, the presence of these relatively large excesses of alkali metal hydroxide in the spray dryer feed solution results in a sizeable decrease in the yield of hydroxyaromatic acid that is obtained when the alkali metal phenate is carboxylated. In addition, when more than about 0.5 percent of excess alkali metal hydroxide is present in the alkali metal phenate, the product is somewhat hygroscopic and difficult to dry, and the spray dried product contains more than the desired amount of water. Like the presence of excess alkali metal hydroxide, the presence of water in the alkali metal phenate adversely affects the yield of hydroxyaromatic acid resulting from the carboxylation of the phenate. As is shown in Equation 1, the alkali metal phenate reacts with water to yield phenol and alkali metal hydroxide.

\[ \text{OM} + \text{H}_2\text{O} \rightarrow \text{OM}\text{OH} \]

When excess alkali metal hydroxide is present during the carboxylation, it reacts with the carbon dioxide to form the corresponding carbonate and water, and the water formed then hydrolyzes the phenate as is shown in Equations 2 and 3.

\[ 2\text{OMOH} + \text{CO}_2 \rightarrow \text{M}_2\text{CO}_3 + \text{H}_2\text{O} \]

\[ \text{OM} + \text{H}_2\text{O} \rightarrow \text{OMOH} \]

The overall reaction that takes place when alkali metal hydroxide reacts with carbon dioxide and alkali metal phenate is represented by Equation 4.

\[ \text{OMOH} + \text{CO}_2 \rightarrow \text{M}_2\text{CO}_3 \]

Since phenol is not carboxylated under the conditions of the Kolbe reaction, the yield of hydroxyaromatic acid is reduced when excess alkali metal hydroxide and/or water is present in the alkali metal phenate that is carboxylated. In the commercial operation of the Kolbe process, the phenol is usually recovered and used in the preparation of additional amounts of alkali metal phenate.

In accordance with this invention, a procedure has been developed for the accurate and rapid determination of the amount of excess alkali metal hydroxide that is present in the aqueous alkali metal phenate solution that is used as the spray dryer feed solution. When this method of determining the alkalinity of the solution is used, adjustments in the relative amounts of the reactants that are used can be made rapidly, and as little as 0 to 0.5 molar percent excess alkali metal hydroxide may be used without danger of decomposition and discoloration of the product occurring during the spray drying operation. As the result of the use of these uniform small excesses of alkali metal hydroxide, the spray-dried alkali metal phenate which is substantially anhydrous can be carboxylated to give improved yields of the corresponding hydroxyaromatic acid.

The novel method of controlling the alkalinity of alkali phenate solutions is based on the observation that the excess alkali metal hydroxide in the alkali metal phenate solution reacts with carbon dioxide in the drying gas according to the following equation:

\[ 2\text{OMOH} + \text{CO}_2 \rightarrow \text{M}_2\text{CO}_3 + \text{H}_2\text{O} \]

In this method, the difference between the carbon dioxide content of the gas that enters the spray dryer and that of the
The gas that leaves the spray dryer is used as a measure of the amount of alkali metal hydroxide that is present in the alkali metal phenate feed solution.

When drying gas having a known and uniform carbon dioxide content is introduced into the spray dryer, there is a direct correlation between the carbon dioxide content of the exit gas and the alkalinity of the feed solution. By determining the carbon dioxide content of the exit gas continuously or at frequent intervals and then adding the amount of phenol or alkali metal hydroxide to the feed solution that is necessary to keep the carbon dioxide content of the exit gas within a predetermined range, it is possible to maintain the percentage of the feed sol- 

The following table. The gas introduced into the spray dryer during this run contained about 0.055 percent of carbon dioxide.

<table>
<thead>
<tr>
<th>Percent CO₂ in exit gas:</th>
<th>0.000</th>
<th>0.002</th>
<th>0.005</th>
<th>0.008</th>
<th>0.010</th>
<th>0.012</th>
<th>0.014</th>
<th>0.016</th>
<th>0.018</th>
<th>0.020</th>
<th>0.022</th>
<th>0.024</th>
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<th>0.028</th>
<th>0.030</th>
<th>0.032</th>
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<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
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</tbody>
</table>

In the practice of this invention, a aqueous alkali metal phenate solution is spray dried by the process described in U.S. Pat. application Ser. No. 584,576. During the spray drying, samples of the exit gas are drawn continuously or peri-

dically from the exit gas stream and optionally from the inlet gas stream and fed to a gas analyzer calibrated to give readings of 0 to 0.5 percent of carbon dioxide. When gas of known carbon dioxide content, such as air, is being introduced into the spray dryer, the measurement of the carbon dioxide content of the inlet gas is usually omitted. For each set of reaction conditions being used, which include, for example, the salt being dried, the concentration of the feed solution, the spray drying condi-
tions, the carbon dioxide content of the inlet gas, and the like, a correlation is established between the carbon dioxide con-
tent of the exit gas and the amount of excess alkali metal hydroxide or phenol in the feed solution. Such a correlation may be established by analyzing samples of the feed solution during spray drying and equating their analyses with the car-
bon dioxide content of the exit gas at the time the samples were taken. A typical correlation between the phenol or sodium hydroxide content of a sodium phenate feed solution and the carbon dioxide content of the gas leaving the spray dryer is shown in the following table. The gas introduced into the spray dryer during this run contained about 0.055 percent of carbon dioxide.

In the practice of this invention, following the determination of the amount of excess phenol or alkali metal hydroxide that is present in the feed solution, sufficient phenol or alkali metal hydroxide is added automatically or manually to the feed solution to bring the carbon dioxide content of the exit gas to the preferred range of about 0.01 percent to 0.025 percent, which corresponds to about 0 to 0.2 percent of excess alkali metal hydroxide in the feed solution.

While the process of this invention is of particular value in the production of sodium phenate, which is used commercially in the preparation of salicylic acid, it can also be used in the production of other alkali metal salts, including alkali metal phenates and alkali metal carboxylates. The phenols whose alkali metal salt solutions may be used as the starting materials in the novel method of this invention may be any mononuclear or polynuclear aromatic compound containing at least one hydroxyl group substituted in the aromatic nucleus. They may also have other nuclear substituents such as alkyl groups, halogen atoms, amino groups, nitro groups, and the like. Illustrative of these phenols are the following: phenol, o-, m-, and p-cresols, p-aminophenol, m-nitrophenol, 2,4-dichlorophenol, pentachlorophenol, 1-naphthol, 2-naphthol, 3-amino-1-naphthol, 4-nitro-1-naphthol, 1-chloro-

2-naphthol, and the like. Alkali metal hydroxide solutions may be used in the practice of this invention include a wide variety of monobasic and polynuclear aromatic and acidic acids, such as hexanoic acid, decanoic acid, citric acid, ethylenediamine tetracetic acid, hydrox-

methyleneethylenediamine triacetic acid, benzoic acid, phthalic acid, tetrachlorophtalic acid, salicylic acid, sulfosalicylic acid, toluenesulfonic acid, and the like. Sodium and potassium are the most commonly used and the preferred alkali metal constituents of the salts; salts of other metals of Group I A of the Periodic Table of the elements may also be used, if desired, in the practice of this invention.

The aqueous alkali metal salt solution that is used as the feed to the spray dryer comprises from about 50 percent to 75 percent by weight of one or more of the aforementioned alkali metal salts and from about 25 percent to 50 percent by weight of water. As is well known in the art, the aqueous salt solutions may be prepared by reacting a phenolic compound or carbox-
ylic acid in solid state, in molten state, or in solution or suspen-
sion in a suitable liquid with an alkali metal hydroxide which may also be in the solid state, in solution, or in suspension. For example, the solution may be prepared by mixing alkali metal hydroxide or carboxylic acid in a concentrated aqueous solution of an alkali metal hydroxide.

As is disclosed in U.S. Pat. application Ser. No. 584,576, the spray drying of alkali metal salts can be carried out in conven-
tional spray drying equipment. Spray dryers generally consist of a means of atomizing the liquid feed, a source of hot gas, a drying chamber, and a means of separating the dry product from the exhaust gases. The spray dryer may be operated with concurrent or countercurrent gas flows. The use of a countercurrent drying gas flow is preferred for the present purposes.

The drying gas that is used in this process must contain no more than about 0.5 percent by volume of carbon dioxide, since when greater amounts of carbon dioxide are present reactions which occur between the alkali metal salt and carbon dioxide yield undesirably byproducts, such as unstable alkali metal phenylcarbonate, which burns in the presence of oxygen. Consequently, both the yields and the quality of the product are adversely affected by the presence of more than about 0.5 percent by volume of carbon dioxide in the gas. Air and other inert gases that contain less than about 0.5 percent by volume of carbon dioxide may be effectively employed as the drying gas in the spray drying step.

In most cases the drying gas enters the drying chamber of the spray dryer at a temperature within the range of about 500° to 900° F. The outlet temperature of the drying gas will range from about 230° to 300° F. It will be understood, how-

ever, that the exact temperature of the drying gas is not criti-
cal, since the required temperature need only be high enough to obtain the desired degree of dehydration and will depend in part upon the residence time of the drying gas in the drying chamber. For most purposes the residence time will vary from about 5 to 30 seconds. When a hotter drying gas stream is em-
ployed, the residence time may be still shorter. In all cases the outlet temperature of the drying gas must be maintained below the decomposition temperature of the particular alkali metal phenate being treated. The spray drying step is ordinari-

ly carried out under ambient pressure conditions. Any of the commercially available gas analyzers that are capable of reporting carbon dioxide contents in the range of 0 to 1.0 percent can be used in the practice of this invention. For example, a Beckman IR Analyzer Model 315 has been used in combination with a Honeywell Single Pen Strip Chart Recorder to measure the alkalinity of spray dried sodium phenate.

The invention may be more clearly understood when it is considered in conjunction with the attached drawing. This
drawing illustrates schematically an apparatus in which a preferred embodiment of the process of this invention may be carried out.

As is shown in the drawing, feed tank 11 contains an aqueous solution comprising 65 percent by weight of sodium phenate and a 0.1 to 0.3 molar percent excess of sodium hydroxide. This solution 12 was prepared by adding an appropriate amount of phenol to weigh tank 13 and an appropriate amount of a 50 percent aqueous sodium hydroxide solution to weigh tank 14 and mixing the phenol and aqueous sodium hydroxide solution in mix tank 15 before adding the resulting solution to feed tank 11. The aqueous sodium phenate solution 12, which was maintained at a temperature of about 200° F. to prevent its solidification in the unheated feed lines, was fed through line 16 to centrifugal atomizer 17, which atomized the feed in a horizontal plane. The droplets of feed solution fell continuously into chamber 18. Line 19 delivered air containing about 0.05 percent by volume of carbon dioxide which had been heated to about 575° F. into chamber 18, and the heated air countercurrently contacted the aqueous sodium phenate droplets and caused them to dry, thereby producing finely divided sodium phenate particles having a particle size range of from about 10 to 110 microns, an average particle size of less than about 70 microns, and a water content of less than about 2 percent by weight. The sodium phenate powder was collected in container 20. Outlet air at a temperature of about 250° F. which contained some entrained sodium phenate particles was passed through line 21 into a cyclone separator 22 and the sodium phenate particles were collected in container 20a. The air was passed through line 23 by means of fan 24 into a water scrubber 25 and cooled before being returned to the process through line 26. Nitrogen was added to the gas through line 27 to replace gas lost during the spray drying process. The gas stream was passed through heater 28 using fan 29 before it was returned to chamber 18. During the process samples of the exit gas were withdrawn from line 23 through line 30 by means of vacuum pump 31 into CO2 analyzer-recorder 32. Optionally, samples of the inlet gas were withdrawn from line 19 through line 33 by means of vacuum pump 34 into the CO2 analyzer-recorder 32.

Whenever the gas analyzer 32 indicated that the carbon dioxide content of the exit gas was not in the range of about 0.010 percent to 0.025 percent, sufficient phenol or sodium hydroxide was added to weigh tanks 13 or 14 to bring the carbon dioxide content of the exit gas to this range.

The spray drying apparatus schematically shown in the drawing corresponds to a Nerco-Niro Spray Dryer Model M-260. This apparatus, operated in the above-described manner, produced about 1100 pounds per hour of sodium phenate that contained 0.1 molar percent to 0.3 molar percent of sodium hydroxide and about 0.1 percent by weight of water when a residence time in chamber 18 of about 10 seconds was used. When this sodium phenate was carboxylated, salicylic acid was obtained in a conversion of 88 percent and a yield of 94 percent.

In the hereinbefore described process, the gas leaving the spray dryer is passed through a cyclone separator and a water scrubber before it is recycled. Nitrogen is added to the gas stream to replace gas lost during the spray drying process. Sufficient air enters the system through leaks in the equipment to maintain the carbon dioxide content of the inlet gas at about 0.055 percent by volume.

In another preferred embodiment of the process, the drying gas which has been heated to a temperature in the desired range is passed into the spray dryer. The exit gas is passed through a cyclone separator and water scrubber and is then discarded. When the drying gas is not recycled, it is preferred that the carbon dioxide contents of both the inlet gas and the exit gas be measured so that an accurate determination can be made of the amount of carbon dioxide that has reacted with the excess phenol or alkali metal hydroxide in the feed solution.

The terms and expressions that have been used are used as terms of description and not of limitation. There is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof. It is recognized that various modifications are possible within the scope of the invention claimed.

I claim:

1. In the process for the production of substantially anhydrous particles of an alkali metal phenate which comprises atomizing an aqueous solution containing about 50 percent to 75 percent by weight of said salt, contacting the resulting spray with a stream of inert gas containing less than about 0.5 percent by volume of carbon dioxide and heated to a temperature in the range of about 500° F. to 900° F. for the time required to effect dehydration and solidification of the alkali metal salt in said spray, and separating substantially anhydrous, finely divided particles of said alkali metal salt from said inert gas stream, the improvement wherein the alkali content of the aqueous alkali metal salt solution is maintained within the range of 0 to 0.5 molar percent by measuring the carbon dioxide content of the inert gas leaving the spray dryer and adding to the aqueous alkali metal salt feed solution the amount of alkali metal hydroxide necessary to maintain the carbon dioxide content of said inert gas within a predetermined range.

2. The process of claim 1 wherein the alkali metal phenate is sodium phenate.

3. The process of claim 1 wherein the alkali content of the aqueous alkali metal phenate solution is maintained within the range of 0.1 molar percent to 0.3 molar percent.

4. The process of claim 1 wherein the carbon dioxide content of the inert gas leaving the spray dryer is continuously monitored.

5. The process of claim 1 wherein the carbon dioxide contents of the inert gas entering the spray dryer and of the inert gas leaving the spray dryer are measured and the difference between these carbon dioxide contents is used as an index of the alkali metal hydroxide content of said spray dryer feed solution.

6. The process of claim 5 wherein the difference between the carbon dioxide content of the inert gas entering the spray dryer and that of the inert gas leaving the spray dryer is used to control the flow of alkali metal hydroxide into said spray dryer feed solution.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,554,265 Dated Jan. 12, 1971

Inventor(s) Gonzalo D. Milian

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, Item 72, The inventor's address should read --Hasbrouck Heights, N.J.--.

Signed and sealed this 20th day of April 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR. WILLIAM E. SCHUYLER, JR.
Attesting Officer Commissioner of Patents