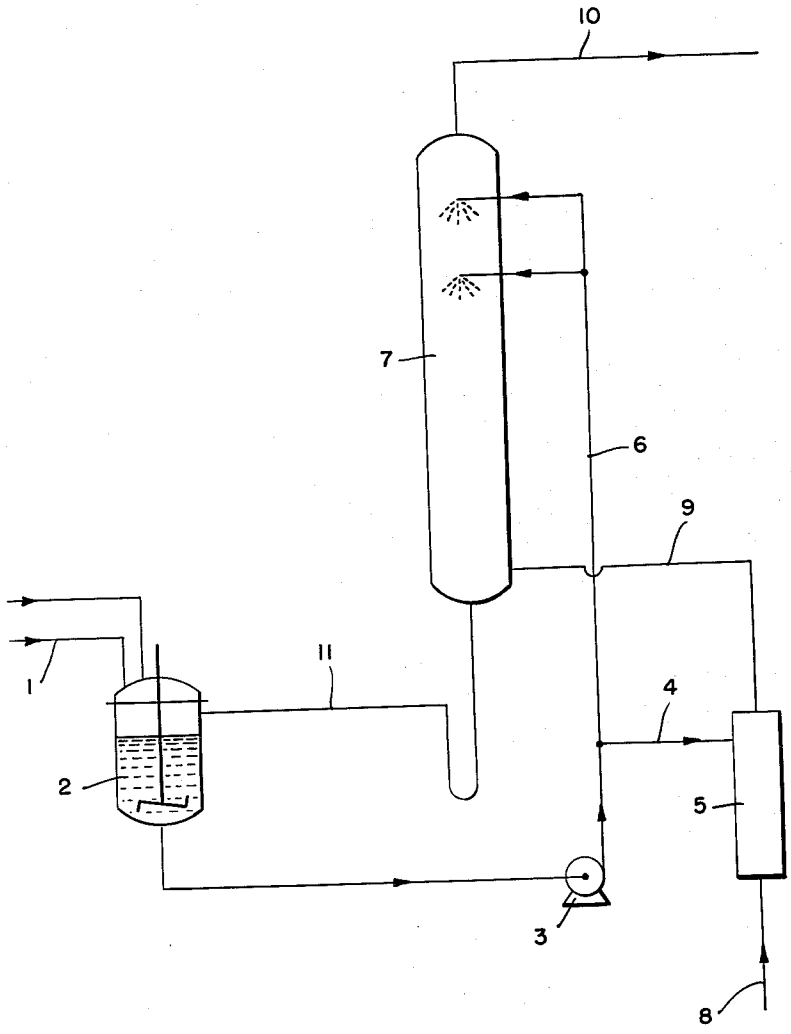
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RECOVERY OF ALKALI METAL SALTS OF BENZENE-CARBOXYLIC ACIDS

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RECOVERY OF ALKALI METAL SALTS OF BENZENE-CARBOXYLIC ACIDS

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This application is a continuation-in-part of our copending application Serial No. 211,113, filed July 19, 1962, now abandoned.

The invention disclosed in the present application relates to a process for the recovery of dry neutral alkali metal salts of benzene-carboxylic acids other than terephthalic acid, suitable for the production of terephthalic acid by thermal rearrangement.

In the thermal rearrangement of neutral alkali metal salts of benzenecarboxylic acids other than terephthalic acid to neutral alkali metal terephthalates it is advantageous to combine the preparation of the initial salts with the liberation of terephthalic acid from the neutral alkali metal terephthalates. This may be carried out for example in accordance with U.S. patent specification No. 2,841,615 by reacting, in a first precipitation step, the neutral alkali metal terephthalate with benzoic acid or with an acid alkali metal salt of a benzenedicarboxylic acid other than terephthalic acid, e.g., with monopotassium phthalate. Thus, acid alkali metal terephthalate, on the one hand and a alkali metal benzoate or the neutral alkali metal salt of the benzenedicarboxylic acid in question, on the other, are obtained in the form of an aqueous solution. In a second precipitation step, terephthalic acid is set free from the acid alkali metal terephthalate by means of benzoic acid, a benzenedicarboxylic acid other than terephthalic acid, or the anhydride of such a benzenedicarboxylic acid. Any acid alkali metal salt of the benzenedicarboxylic acid in question which may have been formed is then employed in the first precipitation step. The above-mentioned aqueous solution of alkali metal benzoate or of the neutral alkali metal salt of the benezenedicarboxylic acid other than terephthalic acid is evaporated. In this way, dry initial salt for the conversion is obtained.

It is extremely important that the initial salt be free from any acid substances, such as benzoic acid or acid potassium phthalate; otherwise the yield of terephthalic acid would be decreased considerably. The 15% to 20% aqueous solutions of neutral alkali metal phthalates which are obtained by the process according to U.S. patent specification No. 2,930,813 have a pH of about 5.6 and cannot therefore be immediately evaporated to give a suitable initial salt. True, if the solution is adjusted to equivalent point by adding caustic alkali solution, preferably caustic potash solution, a suitable initial salt is obtained; but it is difficult in commercial operation always to maintain the equivalence point. If too much caustic alkali solution is added so that the solution contains free alkali metal hydroxide, there results a marked decrease in the yield of terephthalic acid, just as in the presence of acid substances. This risk, involved in the use of caustic alkali solution, may be avoided by adjusting the acid solutions of the initial salt to the equivalence point with potassium carbonate, because an excess of free potassium carbonate in the initial salt does not impair the yield of terephthalic acid. However, in view of the fact that alkali metal hydroxides are much cheaper than potassium carbonate, it is desirable that potassium hydroxide should be used for neutralizing acid constituents in the initial salt solutions.

The recovery of initial salts from their solutions presents a further difficulty. If after the addition of alkali hydroxide or carbonate the solution is first concentrated, then dried in an atomizing dryer by means of burnt gases and the dry salt separated in a cyclone, it is economically advantageous to recover salt dust from the effluent gas and to recycle the salt dust into the reaction. When, however, the usual cloth filters or electrostatic filters are employed, considerable difficulty is encountered, since dipotassium phthalate, for example, is extremely hygroscopic. The salt absorbs moisture from the air and this leads to the blockage of the filter and hence to frequent stoppages in the operation. Such interference can, on the other hand, also be brought about by various types of included catalyst.

It is an object of this invention to provide a process by means of which dry, neutral alkali metal salts of benzenecarboxylic acids other than terephthalic acid are obtained which are suitable for thermal conversion into the salt of neutral alkali metal salts of terephthalic acid. It is another object of this invention to provide a process in which an alkali metal hydroxide is used for neutralizing acid constituents in aqueous solutions of the said neutral alkali metal salts, but in which the presence of free alkali metal hydroxide in the said dry neutral alkali metal salts is safely prevented. It is a further object of this invention to provide a process in which the said neutral alkali metal salts are recovered from their solutions practically completely, i.e., without loss due to entrainment by the gas stream used for drying. It is yet another object of this invention to provide a process in which the above-mentioned neutral alkali metal salts are obtained continuously from their aqueous solutions. It is a still further object of this invention to provide a process in which the measures serving to prevent the presence of free alkali metal hydroxide in the said dry neutral alkali metal salts and to prevent losses of these neutral alkali metal salts due to drying by a gas stream, are combined in such a way that an advantageous over-all effect is achieved. Further objects and advantages will be apparent from the following description in conjunction with the accompanying drawing.

In accordance with this invention these objects are achieved by continuously adding to an aqueous solution of alkali metal salts of benzenecarboxylic acids other than terephthalic acid, the said solution having a pH below the equivalence point of said alkali metal salts, such quantities of alkali metal hydroxide that the pH value of the solution lies 0.05 to 0.9 unit above the point of equivalence, and continuously dividing the solution into two portions, one of which is evaporated to yield the dry neutral salt of the said benzenecarboxylic acid, and the other is brought into intimate contact with carbon dioxide or a gas containing carbon dioxide and then returned to the aqueous solution of the said alkali metal salts of benbenecarboxylic acids other than terephthalic acid, before the said first portion is withdrawn, care being taken to ensure that such an amount of alkali metal hydrogen carbonate is formed in the second portion of the solution by contact with carbon dioxide or a gas containing carbon dioxide as to neutralize the whole excess of alkali metal hydroxide, which brings the pH of the solutions of alkali metal salts of benzenecarboxylic acids other than terephthalic acids to 0.05 to 0.9 unit above the equivalence point.

The process according to this invention, then, consists in a cycle from which neutralized salt solution is continuously withdrawn and into which there is fed continuously a corresponding amount of salt solution having a pH below the equivalence point and alkali metal hydroxide. The salt solution, which is being recycled, is treated with carbon dioxide so that alkali metal bicar-

bonate is formed which neutralizes the excess of free alkali metal hydroxide and thus ensures that the neutralized salt solution withdrawn does not contain any free alkali metal hydroxide.

Preferred benzenecarboxylic acids whose alkali metal salts may be obtained by the process according to this invention are benzoic acid, phthalic acid and isophthalic acid. The aqueous solutions of the alkali metal salts of these acids may be obtained by two-step precipitation as described above, e.g., according to U.S. patent specifications No. 2,841,615 or 2,930,813. The solutions usually contain 25 to 45% by weight of the alkali metal salt in question and have a pH which is below the equivalence point and usually ranges between 4.0 and 7.0. The alkali metal salts are preferably potassium and sodium salts; the proportion of potassium in the total of the said cations should be 60 to 100% so as to achieve high yields.

Among the alkali metal hydroxides to be added sodium hydroxide and particularly potassium hydroxide are preferred. The use of sodium hydroxide is particularly expedient if the sodium content of the salt solution is low. If the proportion of sodium in the total of the alkali metal cations is more than 40%, the use of potassium hydroxide only is to be recommended. The alkali metal hydroxide may be added in solid form or as an aqueous solution, advantageously as a 10 to 50 wt. percent solution. The amount of alkali metal hydroxide may be regulated by means of a pH controller. The temperature of the alkali metal salt solutions is not critical; usually it ranges between 20 and 90° C.

It is an essential feature of this invention that the pH of the alkali metal salt solution is brought to 0.05 to 0.9 unit above the equivalence point by addition of alkali metal hydroxide. Thus, in the case of dipotassium phthalate solutions the pH is adjusted to from 7.95 to 8.8, in the case of potassium benzoate solutions to from 7.35 to 8.2, and in the case of dipotassium isophthalate solutions to from 7.05 to 7.9. The upper limit indicated, viz. 0.9 unit above the equivalence point, is determined by economic rather than technical considerations. If more caustic alkali solution is added, an unnecessarily large amount of alkali metal hydrogen carbonate must be produced by treating the said second portion of the salt solution with carbon dioxide, in order to neutralize the excess of alkali metal hydroxide. If there are alkali metal salts of more than one benzenecarboxylic acid other than terephthalic acid in the solution, the latter is regarded as a solution of that alkali metal salt whose equivalence point is furthest in the alkaline range.

A first portion of the solution—as a rule 1 to 70%, preferably 5 to 25%—to which alkali metal hydroxide has been added is continuously evaporated in conventional manner to obtain the dry salt, if desired in several stages with direct or indirect heating. It is best, at least in the last stage, to use spray dryers in which flue gas is employed. This usually has a temperature between 150 and 400° C. when entering the dryer. In general, 70 to 9 cubic meters (S.T.P.) of flue gas is required per kg. of water to be evaporated, according to the temperature of the flue gas. Conventional catalysts for the conversion to be carried out at a later stage may be added to the said first portion prior to evaporation.

The second portion of the solution to which alkali metal hydroxide has been added is recycled continuously. Before that, however, it is brought into intimate contact with carbon dioxide or a gas containing carbon dioxide. This may be done in conventional manner; the best method is to spray the solution at the upper end of the contact zone into a countercurrent stream of carbon dioxide or a gas containing carbon dioxide. The purpose of the treatment with carbon dioxide is to produce such an amount of alkali metal hydrogen carbonate in the solution (or to dissolve such an amount of carbon dioxide in it) that the excess of alkali metal hydroxide, which has been added to the solutions of the alkali metal salts of the benzenecarboxylic acid in question, is neutralized while the portion treated with carbon dioxide is recycled. The term "alkali metal hydrogen carbonate" as used herein is meant to include the alkali metal carbonate which is formed from the alkali metal hydrogen carbonate proper in amounts varying with the temperature. The pH of the initial solution, viz. 0.05 to 0.9 unit above the equivalence point, is therefore determined by the content of alkali metal carbonate and possibly of alkali metal hydrogen carbonate, but not by alkali metal hydroxide. The salt obtained by evaporation of the said first portion of the solution, then, does not contain any free alkali and is therefore most suitable for the preparation of terephthalic acid.

From the description of the effect of the carbon dioxide treatment it will be apparent that no limiting data can be given on the amount of carbon dioxide or the gas containing carbon dioxide. One factor on which the amount depends is the carbon dioxide content of the gas. If flue gas is used, this content is from 1 to 15% by volume. Obviously, other gases, especially gases having a larger content of carbon dioxide, and pure carbon dioxide are also suitable. The amount further depends on the intensity of the contact between the gaseous and liquid phases. The finer the distribution of the solution sprayed into the gas stream and the longer the period of contact, the smaller the required amount of gas having a given carbon dioxide content. The amount of carbon dioxide or gas containing carbon dioxide required for treating the second portion of solution finally depends on the amount of alkali metal hydroxide added: the higher the pH within the range indicated, the larger the amount required. In practice, usually 6.5 to 15 cubic meters (S.T.P.) of flue gas having a carbon dioxide content of 6 to 15% by volume is used per kg. of the second portion of solution. The temperature at which the carbon dioxide treatment is carried out is not critical. It generally ranges between 20 and 90° C.

The said second portion of the alkali metal salt solution, which has been treated with carbon dioxide, is recycled. It is best to introduce it into the zone where alkali metal hydroxide is added to the initial solution. It may however also be recycled to the aqueous initial solution at a point ahead of, or advantageously after, the neutralization zone, but ahead of the point at which the said first portion is withdrawn.

A modification of the process consists in saturating the off-gas, prior to its entering the wash tower, with water vapor at a temperature higher than that of the gas leaving the wash tower. This means that there is then a partial condensation of water vapor in the wash tower so that the dust particles act as condensation nuclei and can, in consequence, be particularly easily separated. In this case, the salt solution pumped in is merely warmed owing to the condensation heat.

The process according to this invention may be carried out particularly advantageously if the said second portion is treated with the flue gas leaving the evaporator in which the dry alkali metal salt of the benzenecarboxylic acid in question is recovered from the said first portion. In this case the alkali metal salt contained in the flue gas is washed out by the said second portion and thus recovered. Other advantages are that the carbon dioxide content and the heat content of the flue gas are utilized.

The parts specified in the following examples are parts by weight unless otherwise stated. The parts by weight bear the same relation to parts by volume as the kilogram to the cubic meter.

Example 1

In a continuous plant for the manufacture of terephthalic acid by thermal conversion of dipotassium phthalate in the presence of catalysts, an hourly yield of 220 parts of dipotassium phthalate, 10.7 parts of potas-

sium hydrogen phthalate and 2.8 parts of by-products in 1460 parts of water is obtained on working up the reaction mixture. The pH value is 5.6, and the temperature 30° C. This solution is processed in a plant such as is represented diagrammatically in the accompanying drawing. It is first led through feed line **1** into a vessel **2** and automatically adjusted to pH 8.1 by means of a 50% potassium hydroxide solution at room temperature using a pH controller fitted with a control valve. In this way, 5.3 parts per hour of 50 wt. percent aqueous solution of technical grade potassium hydroxide is added.

By means of a pump **3**, part of the solution (12%) is withdrawn through line **4**, while the remainder (88%) is supplied through line **6** to a wash tower 7. 11 parts per hour of cadmium phthalate in the form of an about 45 wt. percent aqueous suspension is added to the portion which has been withdrawn through line **4** and led into dryer **5**. 2,000 cubic meters per hour of a flue gas obtained from the combustion of fuel oil is led into the dryer **5**. When steady-state conditions have been set up, there is withdrawn from the dryer 245 parts per hour of solids in the form of a dry salt, which contains 232 parts of dipotassium phthalate.

13,250 parts per hour of alkali metal salt solution is sprayed into the wash tower **7**. The flue gas leaving the dryer **5** is passed through line **9** into the wash tower **7**. The gas is loaded with salt residues that have not been separated, and enters the wash tower **7** at a temperature of 160° C. The carbon dioxide content of the gas is about 12.5% by volume, its water content about 26% by volume. Owing to heat exchange, the salt solution sprayed in at the top is heated from 30° to 47° C., whereas the flue gas absorbs 50 parts of water vapor per hour and leaves the top of the wash tower **7** through line **10** at a temperature of 47° C. In the wash tower **7**, 6.2 parts per hour of dipotassium phthalate is washed out, and the salt solution absorbs 0.95 part of carbon dioxide.

The salt solution is recycled from the wash tower **7** through line **11** to the vessel **2**.

The salt recovered in the dryer **5** may be thermally rearranged by the method described in Example 1 of German Patent specification 1,144,254. Terephthalic acid is obtained in a yield of 94 to 97% of the theory with reference to dipotassium phthalate.

If only such an amount of caustic potash solution is added to the initial solution that just the equivalence point of dipotassium phthalate is reached (using a pH controller) and the solution is then evaporated, a salt is obtained which contains varying amounts of potassium hydroxide. If such a salt is rearranged in the way mentioned above, terephthalic acid is obtained in a diminished yield. For example, the yield is 87% of the theory if the initial salt contains 4 wt. percent of free alkali metal hydroxide.

Example 2

When a conversion mixture comprising 193 parts dipotassium terephthalate which has been obtained in the manner described in German Patent specification No. 1,014,982 by thermally converting 231 parts of the dry, neutral potassium-sodium salts (of which 8% is sodium salts) of a crude xylene oxidation mixture of isophthalic acid, terephthalic acid, phthalic acid and benzoic acid in the presence of a catalyst and carbon dioxide at 445° C., is worked up to recover the terephthalic acid according to the procedure described in U.S. Patent 2,930,813, an amount of solution of neutral salts is obtained each hour which comprises 134.5 parts isophthalate, 41.5 parts o-phthalate, 44 parts benzoate, 6.5 parts hydrogen isophthalate, and 4.5 parts hydrogen terephthalate in 1,600 parts water. The solution, which has a pH value of 5.9, is pumped contrinuously into vessel **2** of the same apparatus as described in Example 1.

The pH is adjusted to 8.01 by adding a 50% wt. percent aqueous alkali metal hydroxide solution (8 wt. percent of sodium hydroxide, 92 wt. percent of potassium hydroxide). 8.25 parts of the said alkali metal hydroxide solution is required each hour. The addition of this solution is regulated by means of a pH controller.

1,840 parts per hour of the alkali metal salt solution is withdrawn through line **4** and evaporated in the dryer **5** into which 2,400 cubic meters (S.T.P.) per hour of a flue gas obtained from the combustion of oil is introduced from below. 231 parts per hour of a mixture of alkali metal salts, which is well suited for thermal rearrangement to alkali metal terephthalates, is obtained.

13,160 parts per hour of the solution withdrawn from the vessel **2** is sprayed into the wash tower **7**. The flue gas leaving the dryer **5** is passed into the wash tower **7** from below. This gas contains 11 parts by volume of carbon dioxide and 25 parts by volume of water, has a temperature of 140° C., and carries with it 6.2 parts per hour of alkali metal salt from the dryer **5**. The alkali metal salt solution enters the wash tower **7** at a temperature of 45° C. and leaves it at 53° C. All alkali metal salt present in the gas stream is washed out in the wash tower **7**. The temperature of the gas stream leaving through line **10** is 53° C.

On leaving the wash tower **7**, the alkali metal salt solution, which absorbs 0.91 part per hour of carbon dioxide, is recycled to the vessel **2** through line **11**.

What we claim is:

1. A process for the recovery of alkali metal salts of benzene-carboxylic acids other than terephthalic acid which comprises adding to an aqueous solution of alkali metal salts of benzenecarboxylic acids other than terephthalic acid, which solution also contains at least one acid substance selected from the group consisting of benzoic acid and acid alkali metal phthalates and has a pH below the equivalence point of said alkali metal salts, such an amount of alkali metal hydroxide that the pH of said solution is 0.05 to 0.9 unit above the equivalence point of said alkali metal salts, and dividing the solution obtained into two portions, one portion being evaporated for recovery of dry alkali metal salts of said benzenecarboxylic acids and the other portion being brought into intimate contact with a gas selected from the group consisting of carbon dioxide and a gas containing carbon dioxide and then being recycled to said aqueous solution of said alkali metal salts of a benzenecarboxylic acid other than terephthalic acid at a point ahead of that where said one portion is withdrawn, such an amount of alkali metal hydrogen carbonate being produced in said other portion by said contact with said gas that the whole excess of alkali metal hydroxide, which brings the pH of said solutions of said alkali metal salts of benzenecarboxylic acids other than terephthalic acid to 0.05 to 0.9 unit above the equivalence point, is neutralized.

2. A process as claimed in claim **1** wherein said alkali metal salt of said benzenecarboxylic acid is dipotassium phthalate.

3. A process as claimed in claim **1** wherein said one portion of said alkali metal salt solution is sprayed into hot flue gas and thereby evaporated and wherein said flue gas is used as the gas containing carbon dioxide for treating said other portion of said alkali metal salt solution.

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