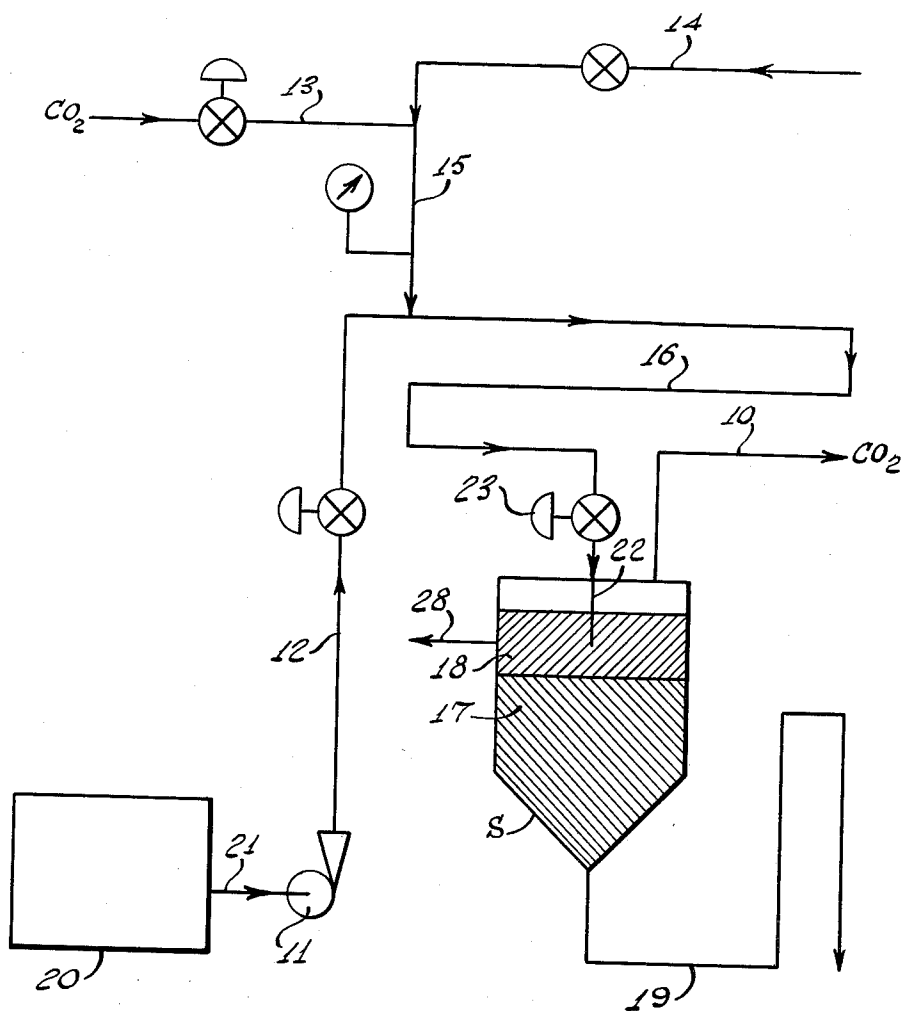


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ALKALI-CONTAINING PHENOL OILS
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PROCESS FOR THE AFTER-CARBONIZATION OF ALKALI-CONTAINING PHENOL OILS

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The present invention relates to the after-carbonization of such phenol oils which are recovered from phenolate liquors or which have been refined by a solution process with caustic alkali solutions, the caustic alkali being thereby converted into alkali metal bicarbonate. In both cases the phenolate liquors are decomposed by treatment with gaseous carbon dioxide, whereby from the alkali phenolate, free phenols are obtained, on the one hand, and alkali metal carbonate solutions, on the other hand. In general, sodium phenolate solutions are used in industrial processes, which yield by decomposition with carbon dioxide a solution of sodium carbonate or bicarbonate, respectively. Such a decomposition process is known as "carbonization" or "saturation."

In the carbonization, the treatment of the phenolate liquor with carbon dioxide is preferably only effected to an extent, that sodium carbonate but no substantial amount of sodium bicarbonate will be obtained. This is done for the reason that upon carbonization which leads to larger amounts of sodium bicarbonate, the disadvantage would be incurred that more carbon dioxide is consumed than is necessary for the decomposition of the phenolate, and that the conversion of the carbonized liquor into caustic soda solution which generally occurs by causticizing with caustic lime, is more difficult and requires a larger amount of chemicals.

Phenol oils obtained from phenolate liquor by carbonization to the extent that carbonates are obtained, contain considerable amounts of dissolved alkali. This content in alkali solution is disadvantageous in the further processing of phenol oils, since, in subsequent distillation, it leads to incrustations and corrosions in the distillation column. Moreover, the alkali content remaining in the phenol oil spells a loss in chemicals, since it cannot be again converted into caustic soda solution. It has therefore been proposed to mix to the alkali-containing phenol oil such an amount of mineral acid, e.g. sulfuric acid, that the alkali content will be neutralized thereby. In this case, the corresponding neutral alkali metal salts of mineral acids will be formed which separate easily as a waste liquor or spent lye from the phenol oil to be treated. In this manner, alkali-free phenol oils are obtained, but in this case, too, alkali contained in the phenol oil will be lost. Furthermore, frequently the treated phenol oils contain free mineral acids which even when present in traces only, will lead to heavy corrosions in the subsequent distillation. The treatment with mineral acids is particularly damaging when the phenol oil contains fatty acids, or fatty acid metal salts which are frequently obtained with phenol oil made from products obtained in the low temperature carbonization of lignites. In this treatment of such phenol oils, free fatty acids are formed from the salts thereof, which pass into the spent lye only to a small extent, whereas the larger portion remains in the phenol oils. As a consequence, in the distillation of such oils very heavy corrosions will occur.

In order to avoid these disadvantages it has further been proposed to treat the alkali-containing phenol oils not with mineral acids, but with carbon dioxide. Contrary to the carbonization mentioned above, the phenolate liquors are in this case treated until bicarbonate formation occurs. A marked reduction of the alkali con-

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tents of the phenol oils will thus be effected. Moreover, phenol oils so treated will not have the corrosive properties similar to those after-treated with mineral acids. The treatment of alkali-containing phenol oils with carbon dioxide is called in the art: "after-carbonization" or "second saturation." The process is carried out by injecting gaseous carbon dioxide preferably in finely divided form into a container wherein the alkali-containing phenol oil is present. The operation is carried out in batches and the injection of carbon dioxide is continued until no more sodium bicarbonate is separated out. It has also been attempted to make the after-carbonization process a continuous one instead of operating in discontinuous manner as described above. For making the process continuous, the alkali-containing phenol oils were allowed to pass from the top through a column charged with solid bodies where carbon dioxide was passed from the bottom of the column to the top in counter-current. However, this mode of operation is very unsatisfactory, because the sodium bicarbonate formed is deposited as a solid which clogs the filling bodies and obstructs the entire column after a short while. The column has therefore to be taken out of operation and the separated solid sodium bicarbonate has to be rinsed out by washing the column with water or with steam.

In order to avoid these disadvantages, it has further been proposed to perform the after-carbonization in the column charged with filling bodies in the presence of a solvent for the sodium bicarbonate. Water is not very well suited for the purpose, because the sodium bicarbonate solution obtained has a specific gravity which is only a little above 1, due to the low solubility of sodium bicarbonate in water.

Consequently, the sodium bicarbonate solution does not separate from the treated phenol oil which has a specific gravity of about 1.05. It has therefore been tried not to use pure water but a solution of neutral salt, for instance 10% sodium sulfate solution which has a specific gravity of at least 1.10. The procedure was to charge phenol oil and sodium sulfate solution simultaneously to the upper end of the after-carbonization column whereas carbon dioxide was blown in counter-current thereto from the bottom. The two liquids intermingle while they trickle down over the filling bodies and the sodium sulfate solution distributed in the phenol oil dissolves the sodium carbonate as it is formed. Clogging by deposits of solid sodium carbonate thus does not occur any longer. The mixture of phenol oil and sodium bicarbonate-containing sodium sulphate solution can easily be withdrawn at the bottom of the column and can be separated by settling into phenol oil, on the one hand, and spent lye, on the other hand. However, this process, too, has its disadvantages. These are, for instance, that it is particularly cumbersome and that it is not easy to recover in a simple manner the sodium bicarbonate contained in the spent lye and to reconvert it into caustic soda solution.

It is an object of the present invention to overcome the disadvantages of the known processes and to provide a method for carrying out the after-carbonization of alkali-containing phenol oil which permits the utilization of the chemicals employed in the process to best advantage and without substantial losses.

It is a further object of the invention to provide a process for carrying out the after-carbonization in a simple and inexpensive apparatus.

Other objects and advantages of the present invention will become apparent from the detailed description hereinafter.

It has now been found that an after-carbonization can be carried out in a simple manner and in continuous operation when the counter-current principle used up to the present is omitted and when the phenol oil and the

gaseous carbon dioxide are instead allowed to react while being passed through an apparatus unidirectionally.

In this case, it is not necessary to use the column charged with filling bodies, but a simple tube will serve the purpose.

The tube may be either set up vertically or it may be horizontally disposed. It is convenient to use a tube or column which is arranged at an angle with respect to the horizontal. Phenol oil and carbon dioxide are fed into the tube at the upper end thereof. Both media pass through the tubes together in the same direction from top to bottom. The after-carbonization effect is all the more effective, the longer the tube. In general, however, a tube of several meters length will be sufficient. Although the sodium bicarbonate will be deposited in solid form, there will not occur any clogging or forming of incrustations, even in a prolonged operation. The solid sodium bicarbonate is deposited in the form of a finely grained sludge slightly mixed with water, and as soon as the reaction mixture has left the tube, the sodium bicarbonate is separated from the phenol oil in practically quantitative amount.

It has further been found that the bicarbonate sludge is particularly well separable from the reaction mixture, when in the tube a temperature of 30° to 50° C., preferably 40° C., is being maintained. It is sometimes advantageous to inject some steam at the upper end of this tube, taking care to keep the amount low enough so that the above-mentioned temperatures will not be exceeded. The after-carbonization tube can be operated practically without excess pressure. However, it was found that it is preferable to operate with a slight excess pressure of 0.5 to 1.5 atmospheres. In this case, the phenol oil and the carbon dioxide are injected into the after-carbonization tube under pressure. The lower end of the after-carbonization tube has to be provided with a pressure release valve in order that the desired pressure can be maintained.

In carrying out the after-carbonization, the amount of carbon dioxide injected per time unit is so chosen that it will be sufficient for converting the alkali-contents in the phenol oil into bicarbonate. However, it is advantageous to operate with some excess carbon dioxide since the after-carbonization effect is particularly satisfactory in that case. When the operation is carried out in this manner, only part of the carbon dioxide injected is used for bicarbonate formation and when pressure is released, the unconsumed carbon dioxide will leave the tube together with the after-carbonized phenol oil and the bicarbonate sludge at the lower end of the tube. In order not to lose this carbon dioxide, it can preferably be used for carbonization of phenolate liquor, for instance of liquor from which a phenol oil to be treated by after-carbonization, is obtained. It is possible to lead the entire amount of carbon dioxide, which is used in the carbonization process, previously through the after-carbonization apparatus.

While in general, a completely empty tube will perform satisfactorily, in some cases it may be advantageous to provide some obstructions in the tube, for instance baffle plates or the like, which will promote the vigorous intermingling of phenol oil and carbon dioxide. In that case, a shorter tube will permit to obtain the same after-carbonization effect which is otherwise only attainable with a much longer but empty tube.

The attached flow sheet illustrates in a general manner the method for carrying out the present invention. The alkali-containing phenol oil for after-carbonization is delivered from a tank 20 through the action of a pump 11 over lines 21 and 12 to a reaction tube 16, where the after-carbonization will be carried out. Carbon dioxide is passed in through a pipe 13 from a source not shown in the drawing. It passes on through pipe 15 and from there likewise enters the reaction tube 16. As illustrated, the phenolate liquor and the carbon dioxide pass through the entire length of tube 16 in the same direction of flow.

If desired, steam may be admitted through a tube 14. All pipes are provided with valves for the control of admitted reactants.

From the reaction tube 16, a short pipe 22 with a pressure relief valve 23 leads into a separator generally designated by S, where the liquid leaving the tube 16 will separate into two layers, an upper layer 18 containing after-carbonized phenol oil, which may leave the separator through a pipe 28, and a lower layer 17 containing waste lye in form of a bicarbonate sludge. The latter can be withdrawn through a discharge pipe 19. Excess gaseous CO₂ will escape from the separator S through a pipe 10 and may be returned into the process.

In the following, the invention will be more fully explained with references to a number of examples but it should be understood that these are given by way of illustration and not of limitation and that many changes and modifications in the details described can be made without departing from the spirit of the invention and the scope of the appended claims.

Example 1

The upper end of a reaction tube similar to tube 16, placed at an angle with the horizontal of about 10 degrees, having a length of 12 meters and a width of 50 mm., is charged hourly with 400 liters of alkali-containing phenol oil having an alkali content of 14.52 g./kg., calculated as Na₂CO₃, and with 3000 liters of carbon dioxide. Both components had been previously heated to 35° C. The relief valve 23 at the lower end of the tube is so adjusted that the pressure in the tube will be one atm. excess pressure. Simultaneously with the phenol oil and the CO₂, 8 kg. low pressure steam of 2 atm. excess pressure are injected into the tube per hour. The temperature in the reaction tube is maintained at 40° C. Through the relief valve, a mixture of phenol oil and bicarbonate sludge is withdrawn which can be easily separated by settling in the separator S into a sludge-like spent lye, and a supernatant phenol oil containing only 5.6 g. Na₂CO₃ per kg. phenol, and which has practically no mechanically admixed sodium bicarbonate therein.

The amount of separated, after-carbonized phenol oil is 385 liters/hour. Practically no excess carbon dioxide leaves the apparatus, since the entire carbon dioxide injected into the process has been used up for bicarbonate formation.

Example 2

The same apparatus is charged with 400 liters phenol oil containing 14.52 g. alkali calculated as Na₂CO₃ per kg. phenol, and with 20,000 liters CO₂ at 1.5 atm. super pressure. The phenol oil is heated to 35° C., the carbon dioxide to 40° C., so that the temperature in the reaction tube will lie between 35 and 40° C. At the lower end of the tube the after-carbonized phenol oil and the bicarbonate sludge are withdrawn through the valve 23 and at the same time 16,000 liters CO₂ are escaping through line 10. The latter is fed to the carbonization step of the phenolate liquor; the phenol oil and bicarbonate sludge are allowed to settle and are then separated from each other. The amount of after-carbonized phenol oil is 380 liters/hour having an alkali content of only 4.3 g./kg. calculated as Na₂CO₃.

Example 3

In the same apparatus, 600 liters phenol oil and 30,000 liters CO₂ are charged hourly, the phenol oil having an alkali content of 16.2 g. per kg., calculated as Na₂O₃. Steam is also added in an amount to maintain the temperature in the reaction tube at 35–40° C., pressure is adjusted at 2 atm. super pressure.

At the discharge end of the tube, in addition to the after-carbonized phenol oil and the bicarbonate sludge, 20,000 liters unreacted CO₂ are withdrawn which are used for the carbonization of phenolate liquor. From the

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separator, 568 liters after-carbonized phenol oil are withdrawn hourly with a content in alkali of 6.1 g./kg., calculated as Na_2CO_3 .

By the expression "alkali-containing phenol oil" in the specification and claims phenol oils are to be understood which contain a certain amount of Na_2CO_3 .

What is claimed is:

1. In the treatment of alkali-containing phenol oil with carbon dioxide for the recovery of phenol free of alkali, the steps of first treating said phenol oil with carbon dioxide to an extent that substantially sodium carbonate will be obtained, separating the phenol oil from said carbonate, and thereafter again treating the phenol oil with carbon dioxide for after-carbonization with substantial formation of sodium bicarbonate, said after-carbonization being performed by passing said phenol oil and said carbon dioxide simultaneously and concurrently through an elongated reaction zone maintained at a temperature rang-

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ing from 30 to 50° C., whereby substantially alkali-free phenol is obtained.

2. The process as claimed in claim 1, wherein the temperature in the reaction zone is maintained at 40° C.

3. The process as claimed in claim 2, wherein the pressure in the reaction zone is maintained at 2 atmospheres excess pressure.

4. The process as claimed in claim 1, wherein the treatment is carried out in the presence of steam.

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