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HALOGENATED COAL ACIDS

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The present invention pertains and contributes to the chemical arts. In particular, it is concerned with the provision of certain halogenated organic compounds. More particularly, this invention has reference to the chlorinated and brominated polycarboxylic acids that are derived from the oxidation of coal and the like carbonaceous materials which, for convenience, are hereinafter referred to as being "coal acids."

Coal acids are known compounds which, as has been indicated, may be derived from the oxidation of coal. The coal acids that are utilized in the practice of the present invention, for example, may be identical with or similar to those which may be obtained by the oxidation with gaseous oxygen, which may be contained in the air, of an aqueous alkaline slurry of a finely divided carbonaceous material selected from the group consisting of coal and coke that has been obtained by the carbonization of coal at temperatures beneath about 700° C. Coal acids that have been prepared by the nitric acid oxidation of suitable carbonaceous materials are also generally satisfactory, as are equivalent synthetic mixtures. Such coals that are of the varieties known as anthracite, bituminous, sub-bituminous and lignite and other low grade coals are generally suitable for the production of coal acids. Satisfactory cokes are those produced according to conventional techniques from coal at a temperature beneath about 700° C. The utilization of higher coking temperatures frequently causes the cokes to be graphitic and rendered unsuitable for conversion to coal acids in satisfactory yields. One suitable method by which coal acids may be prepared has been described in United States Letters Patent Number 2,516,640.

The free coal acids product is a hygroscopic, usually yellowish, essentially water soluble material that is believed to be substantially comprised of various aromatic polycarboxylic acids. The average molecular weight of the coal acids that are ordinarily obtained is generally from about 200 to 300; frequently being in the neighborhood of 250–270. Their average equivalent weight is generally about 80. It is seldom less than 70 or more than 90. The coal acids ordinarily appear to have an average of 2.5 to 5 carboxylic group per molecule with an apparent average of 3 to 4 being common. While their exact chemical nature and constitution may be somewhat conjectural, they evidently contain considerable quantities of tri- and tetra-carboxylic benzene acids as well as aromatic acids having more complex nuclei. Frequently, for example, the greatly preponderant proportion of aromatic nuclei obtained in coal acids prepared in the described fashion have been found to consist of methylnaphthalene, benzene, biphenyl, naphthalene, phenanthrene, benzophenone and various alkyl benzene, including toluene, nuclei.

It is the principal objective of the present invention to provide, as new and useful compositions of matter, halogenated coal acids, particularly the coal acids that have been halogenated with a halogen selected from the group

of halogens of atomic number from 17 to 35, i.e. chlorine and bromine.

According to the present invention, halogenated coal acids may be obtained by dissolving the free coal acids in water so that the resulting aqueous solution has a concentration between about 5 and 40 percent by weight (preferably between about 10 and 25 percent by weight); then subjecting the coal acids in aqueous solution to the action of a halogenating agent, preferably free chlorine or bromine, at a temperature from about 20 to 95° C. (advantageously, not in excess of 60° C.) while maintaining the reaction mass at a pH in the range from about 3 to 9 (beneficially in the acidic range from about 4 to 7) until the desired content of combined halogen has been obtained in the halogenated coal acids product. Most advantageously, the aqueous solution of the free coal acids may be neutralized with an alkali metal hydroxide (such as sodium hydroxide) prior to halogenation so that initially the solution has a neutral or slightly alkaline pH of about 7 or so and the incipient halogenation is accomplished on the dissolved coal acids in an alkali metal salt form. The halogenated coal acids may be recovered in any desired manner from the reaction mass subsequent to their halogenation after the reaction mass has been acidified to a pH of 1 or so. Conveniently the halogenated coal acids product may be removed from the acidified reaction mass by solvent extraction techniques, using such solvents as methyl ethyl ketone and the like for the purpose. The halogenated coal acids are then isolated from solution in the extracting solvent by conventional distillation or stripping techniques.

Any desired content of combined halogen up to nearly the upper theoretical limit may be effected in the foregoing manner. Of course, the particular halogen (or mixture thereof) involved determines to a great extent the content of combined halogen that may be achieved in the product. When chlorinated coal acids are involved, the halogenated product may advantageously contain up to about 35 percent by weight, more advantageously from about 10 to 30 percent, of combined halogen, based on the weight of the composition. Brominated coal acids may beneficially contain from about 10 to 45 percent by weight of the combined bromine. The time that is required to halogenate the coal acids to a desired combined halogen content varies with the temperature that is employed, the pH that is maintained in the solution, the quantity of the halogenating agent that is utilized, and, as is apparent, the content of combined halogen that is desired to be finally obtained in the substituted product. When the reaction is conducted at temperatures lower than those in the indicated ranges, it may be found to proceed at a slower rate than is desirable. At temperatures higher than those indicated, an intolerably high proportion of the coal acids may be found to be destroyed. In this concention, even at temperatures between 60 and 95° C., greater destruction of the coal acids than is desirable may be encountered. Hence, the preferred indicated lower temperature range may beneficially be utilized for conducting the reaction. If the solution being halogenated is maintained at a pH that is either too high or too low, the rate of halogenation is generally found to be slower than required for practical operations.

Although solutions of the coal acids that are more dilute than 5 percent by weight may be halogenated, the volumetric efficiency of the reaction is undesirably lower at such low concentrations. At starting concentrations of the dissolved free coal acids higher than those indicated, difficulty may be encountered with precipitation of the acids at the commencement of the reaction. For this reason, it is preferred to operate with aqueous solutions which are prepared so as to have concentrations of the

dissolved free coal acids that are not greatly in excess of about 25 percent by weight.

The halogenated coal acids products of the present invention are generally water soluble materials that also have better solubility in various organic materials (such as mixtures of glycols, and fatty acids) than do the unmodified free coal acids. They are generally hygroscopic, yellowish to brown colored powders having apparent bulk densities less than one gram per cubic centimeter. They are found to be soluble in water, acetone and methanol; partly soluble in ethyl acetate; and insoluble in benzene, petroleum ether and carbon tetrachloride. The molecular weight of the halogenated coal acids obviously depends upon that of the starting material and the extent of halogenation involved, as well as the particular halogen that is substituted in the free coal acids. Their average equivalent weight is generally somewhat higher than that of the free coal acids. The substitution of the halogen is believed to occur on both the nucleus and the carboxylic substituents of the coal acids molecules. Frequently about commensurate degrees of nuclear and side chain halogenation are obtained in the products of the present invention. In addition to many other uses, the halogenated coal acid products of the present invention, particularly the chlorinated derivatives, have marked biological activity and are found to have excellent effectiveness against microorganisms especially, for example, as fungicides.

The invention will be further illustrated in and by the following examples which are not intended to be limiting thereof and wherein, unless otherwise indicated, all parts and percentages are to be taken by weight.

Example 1

About 50 grams of free coal acids having an average molecular weight of about 270 and an average equivalent weight of about 83 were dissolved in 221 grams of distilled water. The resulting solution was filtered in order to remove about 1.5 grams of relatively insoluble material. The filtrate was then neutralized with 50 percent caustic (NaOH) aqueous solution to adjust its pH to about 7. The color of the neutralized solution had a numerical rating of about 15 on the Gardner Color Scale.

Elemental chlorine was then sparged into the neutralized solution. Within 7 minutes after the initial introduction of chlorine, the temperature of the reaction mass increased from an initial value of about 28° C. to a temperature of about 35° C. at which level it remained for about 45 minutes. After one hour of reaction, the temperature declined to about 32° C. At this point the pH of the reaction mass was found to be about 3.5. Twenty-eight ml. of the 50 percent caustic solution were then added and the chlorination continued at the same rate. After 22 minutes of the continued chlorination, the temperature rose to about 45° C. and then fell gradually to about 32° C. (within an additional 15 minute period) at which time additional caustic was again added. The chlorine addition was then continued until the temperature cycle again repeated, at the end of which the pH was again adjusted with the caustic solution. After a number of neutralizations with caustic and chlorine additions, a point was attained where very little heat was generated by the caustic neutralization. At this point, which was about 7 hours after the initial introduction of chlorine, the reaction was terminated. The highest temperature that had been reached during the entire chlorination was about 49° C. A total quantity of about 124 ml. of the caustic solution had been used. At the termination of the reaction, the reaction mass containing the chlorinated coal acids in aqueous solution had a pH of about 6.6 and a Gardner Color Number between 8 and 9.

About 22 ml. of concentrated sulfuric acid (H_2SO_4) was then added to the halogenated reaction mass. The pH of the acidified solution was about 0.4. The acidified solution was then twice extracted with separate volumes of methyl ethyl ketone to obtain two separate quantities of the chlorinated coal acids in methyl ethyl ketone solution. The methyl ethyl ketone solutions were then combined and the solvent stripped off under vacuum. About 51 grams of chlorinated coal acids were thereby obtained. The chlorinated product had an equivalent weight of about 111. It was found to contain about 28.1 percent of combined chlorine.

Example 2

In a manner similar to that described in the foregoing example, about 300 parts of coal acids similar to those employed in Example 1 were dissolved in 1200 parts of distilled water and filtered to remove insoluble materials. The pH was adjusted to 7 with 50 percent aqueous caustic solution. The neutralized solution was then chlorinated by sparging free chlorine therethrough. The chlorination was continued for about 10.5 hours at an average temperature of 54° C. During this period a total of 340 parts of free chlorine and 280 parts of NaOH were employed. The reaction mass, after termination of the reaction, was extracted three times with methyl ethyl ketone to recover the chlorinated coal acids. The resulting solutions were mixed and stripped under vacuum to yield about 244 parts of chlorinated coal acids containing about 12.8 percent of combined chlorine. The chlorinated coal acids product was a yellowish colored solid.

Example 3

The general procedure of the first two examples was followed to chlorinate about 50 grams of free coal acids of the same type as used in the foregoing which were dissolved in 200 grams of water, with the exception that the chlorination was conducted at an average temperature of 94° C. At the end of about 3.4 hours the reaction was terminated and about 25 grams of chlorinated coal acids were recovered in the above indicated manner. The chlorinated coal acids product contained about 22.8 percent by weight of combined chlorine and had an equivalent weight of 94.

Example 4

The procedure of Example 3 was repeated to chlorinate about 80 grams of free coal acids that were dissolved in 320 grams of water with the exception that the average temperature of the reaction was about 49° C. and the chlorination was continued for a 14 hour period. The chlorinated product contained about 27.7 percent of combined chlorine and had a molecular weight of 297.

Example 5

The foregoing procedure was essentially repeated with a 15 percent aqueous solution of 600 grams of free coal acids that had been filtered and neutralized. The dissolved coal acids were chlorinated for 8.8 hours at an average temperature of 50° C. About 414 grams of a chlorinated coal acids product was recovered. The halogenated acids product contained about 12.4 percent of combined chlorine and had a molecular weight of about 328.

Example 6

The procedure of Example 5 was repeated to chlorinate about 50 grams of free coal acids in a 10 percent aqueous solution for 3.7 hours at an average temperature of 24° C. to give a chlorinated product containing about 17.4 percent combined chlorine with an equivalent weight of 107.

Upon being tested according to conventional procedures for biological activity, the product was found to effectively inhibit the growth of such organisms as *Aerobacterium aerogenes; Erwinia carotovora; Salmonella typhosa; Staphylococcus aureus; Aspergillus terreus* and *Penicillium digitatum* when incorporated in the culture

medium as an antimicrobial agent at about 0.1 percent concentration.

Example 7

The procedure of Example 6 was repeated excepting to conduct the chlorination for a total period of 6 hours at 42° C. About 48 grams of chlorinated coal acids were obtained having a combined chlorine content of about 30.5 percent.

Example 8

When the general procedure that is set forth in the foregoing examples is repeated, excepting to perform the halogenation with elemental bromine, equivalent results and commensurate products are obtained. The brominations may frequently require a longer period of time than the corresponding chlorinations. Mixed halogen products can also be obtained by performing the halogenation with either mixtures of chlorinating or brominating agents or by separately performing the chlorination and halogenation in any desired sequential order.

Example 9

Using an apparatus in which a pH reading could be continuously obtained, a charge of about 1 equivalent of free coal acids in 900 grams of water was prepared. The free coal acids product had an average molecular weight (as determined by boiling point evaluation techniques) of about 284, an apparent equivalent weight of about 84.6, and upon analysis, was found to contain about 54.36 percent by weight of combined carbon; about 3.10 percent by weight of combined hydrogen; about 0.52 percent by weight of combined nitrogen; and about 0.16 percent by weight of combined sulfur. The carbon-to-hydrogen ratio in the free coal acids product was about 1.46:1. It had an average functionality, or number of carboxylic groups per molecule, of about 3.36.

The prepared coal acids solution was neutralized with about a 90 ml. volume of a 40 percent aqueous sodium hydroxide solution. After the initial neutralization, about 122 grams of chlorine and 185 ml. of the 40 percent sodium hydroxide solution were added uniformly over a period of about 5.5 hours, while the reaction mass was maintained at a temperature between about 18 and 24° C. The pH of the reaction mass was kept between about 4.7 and 7.5 during the reaction period. After the termination of the reaction, the reaction mass was acidified with concentrated sulfuric acid to a pH of about 1 whereupon it was extracted three times with separate 200 ml. portions of methyl ethyl ketone. The methyl ethyl ketone extractant was then stripped off under vacuum to give about 64 grams of a tan powder that had a combined chlorine content of about 14.2 percent and an equivalent weight of about 106. The dried sample had an apparent bulk density of about 0.80 gram per cubic centimeter. The above product is found to have about the same biological activity and other utilities as that of Example 6.

Example 10

Using the procedure of Example 9 and employing similar free coal acids product for the reaction, a starting solution of about 1.5 equivalents of the free coal acids dissolved in about 1040 grams of water was prepared. The coal acids solution was initially neutralized with about 110 ml. of the 40 percent aqueous solution of sodium hydroxide. After the initial neutralization, about 250 grams of bromine and 90 ml. of the 40 percent sodium hydroxide solution were uniformly added over a period of about 4½ hours while the reaction mass was maintained at a temperature between about 22 and 36° C. and a pH of from 5.3 to 7.1. At the termination of the reaction, the reaction mass was acidified with concentrated sulfuric acid to a pH of about 1. It was then extracted with methyl ethyl ketone and the extract dried to give about 138 grams of a dark brown powder product that contained about 21.4 percent of combined bromine and had an equivalent weight of about 106. The brominated coal acids product had an apparent bulk density of about 0.73 gram per cubic centimeter.

Since certain changes and modifications in the practice of the present invention can readily be entered into without substantially departing from its intended spirit and scope, it is to be fully understood that the foregoing description and specification be interpreted and construed as being merely illustrative of the invention which in no sense or manner is to be understood as being limited to or restricted by the specific preferred embodiments therein described but is to be viewed as comprehending the scope and purview that is set forth and defined in the hereto appended claims.

What is claimed is:

1. Halogenated coal acids containing up to about 45 weight percent, based on the weight of the composition, of combined halogen wherein the halogen substituents are selected from the group of halogens consisting of chlorine, bromine and their mixtures; said coal acids being the water-soluble, mixed aromatic polycarboxylic acids that are the products of the oxidation of carbonaceous materials, which acids typically have an average molecular weight of from 200 to 300, and average apparent equivalent weight of from 70 to 90, and contain an average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecule.

2. Halogenated coal acids containing up to about 45 weight percent, based on the weight of the composition, of combined halogen wherein the halogen substituents are selected from the group of halogens consisting of chlorine, bromine and their mixtures; said coal acids being the water-soluble, mixed aromatic, polycarboxylic acids that are the products of the oxidation of coal, which acids typically have an average molecular weight of from 200 to 300, and average apparent equivalent weight of from 70 to 90, and contain an average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecule.

3. Halogenated coal acids as delineated in claim 2 and containing between about 10 and 35 percent by weight, based on the weight of the composition, of combined chlorine.

4. Halogenated coal acids as delineated in claim 2 and containing between about 10 and 45 percent by weight, based on the weight of the composition, of combined bromine.

5. Halogenated coal acids in accordance with the composition that is set forth in claim 2, wherein the combined halogen is chlorine.

6. Halogenated coal acids in accordance with the composition that is set forth in claim 2, wherein the combined halogen is bromine.

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