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PROCESS OF PRODUCING POLYCARBOXYLIC ACIDS

Otto Grosskinsky and Walter Thürauf, Dortmund-Eving, Germany

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The present invention relates to a new process of producing polycarboxylic acids and more particularly to a method of extracting low molecular weight polycarboxylic acids from the crude oxidation product produced by the thermal oxidation of carbonaceous matter oxidized by means of such oxidizing agents as nitric acid and the like, said crude oxidation product also containing high molecular weight polycarboxylic acids.

Upon subjecting carbonaceous matter such as fossil or more recent solid combustible materials such as bituminous coal, lignites, peat and the like or their carbonization products such as coke, tar, pitch, etc. to a thermal treatment with oxidizing agents such as nitric acid, chromic acid, permanganate, or oxygen or air under superatmospheric pressure in an alkaline medium, a raw product is obtained which consists essentially of non-converted starting material, non-converted oxidizing agents, and dark-brown or brownish-black colored oxidation products as well as white, yellow, and orange colored oxidation products. In addition the crude oxidation products will generally contain the mineral constituents of the starting material.

The above mentioned light colored oxidation products which are essentially benzene carboxylic acids, i. e. monocyclic aromatic polycarboxylic acids and nitro-compounds of benzene, in the event that nitric acid is used as the oxidizing agent, are commercially valuable. However, the problem of isolating these products in a simple and economical manner has until the present not been suitably solved.

A known method consists in extracting the crude product with suitable organic solvents which dissolve the light colored molecular constituents so that the solution may be separated from the solid matter by filtration. Another method comprises the esterification of the crude product and the distillation of the mixtures of esters, the esters of the low molecular weight carboxylic acids distilling-off first. Still another method comprises subjecting the crude oxidation product to sublimation whereby the low molecular weight acids are sublimated out first. In all of these methods the dark colored oxidation products remain as a residue and may be returned for further oxidation along with the non-converted starting material.

Of the above mentioned separation methods, the extraction method by means of organic solvents is the simplest, yielding the best results. However it has been observed that this method results in products free from objection only when repeatedly applied because the dark colored oxidation products, namely the high molecular weight polycarboxylic acids, are not completely insoluble in any solvent which is utilized as selective for the low molecular weight polycarboxylic acids.

It is therefore an object of the present invention to provide a process of extracting low molecular weight polycarboxylic acids from the crude reaction product obtained by a thermal oxidation of carbonaceous matter, the crude reaction products containing low molecular weight

polycarboxylic acids and high molecular weight polycarboxylic acids, said process resulting in the obtention of substantially pure low molecular weight polycarboxylic acids.

It is another object of the present invention to provide a process of separating low molecular weight polycarboxylic acids from a mixture of the same with high molecular weight polycarboxylic acids which process results in practically perfect selection of the low molecular weight polycarboxylic acids.

It is still a further object of the present invention to provide a process of separating low molecular weight polycarboxylic acids i. e. monocyclic aromatic polycarboxylic acids from a crude reaction product containing the same and also containing high molecular weight polycarboxylic acids whether said crude reaction product is in dry state or in a form of an aqueous mass wherein the low molecular weight polycarboxylic acids and the high molecular weight polycarboxylic acids are in aqueous solution.

With the above objects in view, the present invention mainly comprises the steps of subjecting the crude oxidation product to an extraction treatment with at least one polar organic solvent for both the monocyclic aromatic and the high molecular weight polycarboxylic acids so as to cause dissolution therein of the polycarboxylic acids, treating the thus formed solution of the monocyclic aromatic and high molecular weight polycarboxylic acids in the polar organic solvent with water, thus causing dissolution of the monocyclic aromatic polycarboxylic acids in the water, the high molecular weight polycarboxylic acids not being dissolved in the water, thereby forming a mixture including an aqueous solution of the monocyclic aromatic polycarboxylic acids, separating the aqueous solution of the monocyclic aromatic polycarboxylic acids from the remainder of the mixture; and recovering from the separated aqueous solution substantially pure monocyclic aromatic polycarboxylic acids.

It is preferable according to the present invention to utilize a water-immiscible polar organic solvent, being a solvent for both the low molecular weight polycarboxylic acids and the high molecular weight polycarboxylic acids so that the aqueous solution of the low molecular weight polycarboxylic acids obtained upon mixing water with the polar organic solvent solution of both the low and the high molecular weight polycarboxylic acids may be easily separated from the polar organic solvent. The utilization of a water-immiscible polar organic solvent causes the aqueous solution to form a separate layer from the polar organic solvent, this layer easily being separated from the remainder of the mixture by means of a separatory funnel or any similar device.

According to another preferred embodiment of the present invention it is possible to utilize a water-miscible polar organic solvent. The difficulty of separating the aqueous solution of the low molecular weight polycarboxylic acids from the polar organic solvent and from the high molecular weight polycarboxylic acids may be overcome by either of the following methods or by a combination of these methods: One method of overcoming this difficulty is to add an organic substance to the polar organic solvent either before the polar organic solvent is mixed with the crude oxidation product or after formation of the polar organic solvent solution of the low and the high molecular weight polycarboxylic acids (before mixing the same with water or after mixing the same with water), which organic substance has the ability of annihilating the water-miscibility of the polar organic solvent. An organic substance having this ability is, for example, kerosene. The organic substance which itself is not a solvent for the polycarboxylic acid apparently forms a solution with the polar organic solvent and

due to the presence of this organic substance, i. e., kerosene, in the polar organic solvent, the miscibility of the polar organic solvent is destroyed. This, therefore, allows for separation of the aqueous solution of the low molecular weight polycarboxylic acids from the mixture in the same manner as if a water-immiscible polar organic solvent were utilized.

A second method which obviates the difficulty of utilizing a water-miscible polar organic solvent is the addition of a soluble electrolyte to the water either before or after the water is added to the polar organic solvent solution. This electrolyte, i. e., sodium chloride, has the effect of salting-out the water-miscible polar organic solvent from the water.

The process of the present invention is based on our discovery that the low molecular weight polycarboxylic acids act as intermediary agents with respect to the solubility of the high molecular weight polycarboxylic acids in the polar organic solvent for both the low and the high molecular weight polycarboxylic acids; and that when water is added to a polar organic solvent solution of both low and high molecular weight polycarboxylic acids, the dissolving equilibrium in the polar organic solvent solution is broken and the more readily water-soluble low molecular weight polycarboxylic acids are transferred substantially into the aqueous phase wherein they are dissolved, whereas the high molecular weight polycarboxylic acids are not dissolved in the water. The high molecular weight polycarboxylic acids either remain dissolved in the polar organic solvent liquid phase or they are precipitated in the aqueous phase.

The effect obtainable, as to the percentage of low molecular weight polycarboxylic acids dissolved in the water and as to whether the high molecular weight polycarboxylic acids are precipitated in the aqueous phase or remain dissolved in the polar organic solvent liquid phase depends upon the nature of the solvent or solvents utilized (i. e. the solubility of the high molecular weight polycarboxylic acids in the particular solvent without the presence of low molecular weight polycarboxylic acids), the ratio of the amounts of water and organic solvent, the concentration of the mixture of polycarboxylic acids in both liquids and the temperature. The percentage of low molecular weight polycarboxylic acids dissolved in the water may be raised by repeating the operation, i. e. by repeatedly extracting the organic liquid phase with water; and vice versa, repeatedly extracting the aqueous phase with polar organic liquid solvent.

According to the process of the present invention, therefore, the polar organic solvent solution is preferably repeatedly extracted with water to form aqueous solutions of the low molecular weight polycarboxylic acids, which solutions are separated from the rest of the mixture of polar organic solvent and high molecular weight polycarboxylic acids and from which aqueous solutions the substantially pure low molecular weight polycarboxylic acids are finally recovered. The low molecular weight polycarboxylic acids may be recovered separately from each of the aqueous extracts or all the aqueous extracts may first be combined and the low molecular weight polycarboxylic acids then recovered from the combined aqueous solution.

The light colored low molecular weight polycarboxylic acids may be recovered in substantially pure condition from the aqueous solutions containing the same by simple evaporation of the water from the solution. The dark colored high molecular weight polycarboxylic acids which generally remain in the organic solvent may be returned to the oxidation process or utilized in any other way after separating the organic solvent therefrom by distillation.

When treating the crude oxidation product with the organic solvents different ways of proceeding are applicable. On the one hand, the treatment can be effected by employing a comparatively small amount of the solvent, so that a more or less liquid pulp results which is

treated with water according to the present invention, whereupon either of the phases formed is worked up separately. On the other hand, a good deal of solvent may be applied offering the chance of filtering-off the insoluble matter and subsequently treating the filtrate with water. At any rate there is the choice between directly working up the oxidation product not yet freed from mineral substances and non-converted matter, or first separating the aforesaid impurities, that is, first distilling off any residual nitric acid and immediately treating the entire residue of distillation with the organic solvent, or else separating the insoluble matter from the crude oxidation mixture, either before or after the treatment with the organic solvent. An immediate removing of the insoluble residue from the reaction mixture offers the advantage of dispensing with carrying these ballasting substances through the following stages, which would of course necessitate a special manipulation (filtration or the like).

When utilizing nitric acid as the oxidizing agent for the carbonaceous matter, the crude oxidation products will contain varying amounts of nitrophenols such as picric acid which may pass partially into the aqueous solution when extracting with water, thereby contaminating the final products. This may be prevented by first extracting the nitrophenols from the crude oxidation product before treatment with the polar organic solvent by means of a selective solvent for the nitrophenols, benzene, chloroform or ethylene trichloride. When subsequently extracting with water, the picric acid remains in the organic liquid phase. It is also possible to mix the aqueous extract with benzene or another selective solvent to remove the picric acid from the aqueous extract.

For the best operation of the process of the present invention the oxidation product should be present as free compounds i. e., free carboxylic acids. Therefore, if the oxidizing treatment is carried out in an alkaline medium, the crude oxidation product should first be acidified. On the other hand, if the oxidizing treatment is carried out by means of strong mineral acids, the excess acid should be removed. If nitric acid is used, it is simple to remove the excess acid by distillation. Other mineral acids may be removed by the addition of alkaline substances to the reaction mass.

The crude oxidation product obtained by the thermal oxidation of the carbonaceous matter may be in either dry state or in the form of an aqueous mass wherein the polycarboxylic acids are in aqueous solution. In the event that the crude oxidation product is in the form of such aqueous mass, the process of the present invention as to the manipulative steps is practically the same as above described. For example, the aqueous mass including the aqueous solution of the polycarboxylic acids is mixed with either a water-immiscible polar organic solvent for both said low and high molecular weight polycarboxylic acids or with a water-miscible polar organic solvent for both the low and high molecular weight polycarboxylic acids which has either been rendered water-immiscible by mixture with an organic liquid substance adapted to annihilate the water-miscibility thereof or is later rendered immiscible by such liquid organic substance or by addition of an electrolyte to the water which has the effect of salting-out the organic solvent from the water. In either case, the addition of the polar organic solvent results in a dissolution therein of mainly high molecular weight polycarboxylic acids, the low molecular weight polycarboxylic acids remaining for the most part in the aqueous solution.

The formed polar organic solvent solution of mainly high molecular weight polycarboxylic acids is then separated from the remainder of the mass and is then treated to an extraction process with water to remove any dissolved low molecular weight polycarboxylic acids from the organic solvent. The low molecular weight polycarboxylic acids are then recovered from both the original

aqueous solution which was extracted with the polar organic solvent and from the extract aqueous solution obtained by extracting the polar organic solvent solution with water. The aqueous solutions may be worked up separately for the recovery of the low molecular weight polycarboxylic acids therefrom, or they may be combined and then worked up together.

It is generally preferable, according to the present invention, to subject the crude oxidation product to repeated extractions with the polar organic solvent in order to obtain the best results. If the oxidation product is dry, the repeated extractions with polar organic solvent is desirable in order to remove all of the polycarboxylic acids, both high and low molecular weight. In the event that the original crude oxidation product is in the form of an aqueous mass, the repeated extractions with polar organic solvent is desirable in order to remove mainly substantially all of the high molecular weight polycarboxylic acids. The low molecular weight polycarboxylic acids removed by the polar organic solvent from the aqueous mass along with the high molecular weight polycarboxylic acids may be recovered from the polar organic solvent solution by treatment with water as above described.

It is further preferable according to the present invention to extract the low molecular weight polycarboxylic acids from the polar organic solvent solution of the low and the high molecular weight polycarboxylic acids by repeated extraction treatments with water. Repeating of the water extractions resuls in practically complete removal of the low molecular weight polycarboxylic acids from the organic solvent solution. The resulting aqueous extracts may either be worked up separately or may be combined and then worked up for the recovery of the low molecular weight polycarboxylic acids therefrom.

The process of the present invention is applicable to any polar organic solvent for both the low and the high molecular weight polycarboxylic acids. As stated above it is preferable to utilize water-immiscible polar organic solvents, though water-miscible polar organic solvents may also be utilized as above described by annihilating the water-miscibility of the same. It is also possible to utilize mixtures of solvents as well as individual solvents. The only other requirement of the solvent is that it be chemically non-reactive with the substances present in the crude oxidation product, at least under the conditions of operation.

Suitable polar organic solvents for both low and high molecular weight polycarboxylic acids include some aliphatic, aromatic and alicyclic alcohols, ketones, ethers, esters, aldehydes and the like. The solvents may also contain sulfur, nitrogen and other hetero-atoms in the molecules. The following are some specific solvents which may be utilized, the present invention not being limited to the particular solvents mentioned: cyclohexanone, tetrahydrofurane, cyclohexanol, methylcyclohexanone, methylcyclohexanol, diethylketone, methylethylketone, normal butanol, secondary butanol, isobutanol, and the like.

Organic liquid substances which may be utilized to annihilate the water-miscibility of the polar organic solvent include, but are not limited to, benzene, gasoline, chloroform, ethylene trichloride and the like. Any water-soluble electrolyte may be utilied to salt-out the polar organic solvent from the water, i. e. sodium chloride or any other salt.

It is evident that thanks to the high water solubility of the low-molecular weight carboxylic acids, the complete extraction of said acids from the aqueous reaction liquid is extraordinarily difficult. When employing liquid solvents, such as cyclohexanone, showing a distinct selecting property for the high-molecular dark-colored constituents, even a subsequent extraction of the low-molecular constituents from the organic liquid phase containing the high-molecular constituents may be dispensed with. In this case it is suitable to keep low the ratio of the organic liquid phase to the aqueous phase in order to have the lowest possible quantity of low-molecular weight acids in the organic liquid phase. Of course, this manner of proceeding is advantageously applied only to those oxidation products whose percentage of dark-colored high-molecular products is not too high. When extracting the aqueous solution of such an oxidation product with $\frac{1}{10}$ of its volume of cyclohexanone, an aqueous solution remains which is particularly rich in low molecular constituents. Should a still higher degree of purity be desired, the extraction with cyclohexanone may be repeated. Hence it follows that for the purpose of eliminating the low-molecular weight carboxylic acids from their acid reaction liquids it is essentially important to choose a solvent which is immiscible with the almost acid reaction liquid and shows good dissolving properties for dark-colored high-molecular carboxylic acids.

The extraction with water offers still another advantage. When carrying out said extraction repeatedly, it becomes apparent that parts of the dark-colored products gradually pass into the aqueous phase, so that it is possible to separate more or less light-colored products, according to the quality of the final product desired. The fractions obtained hereby may also be worked up separately. When esterifying the fractions obtained from the organic liquid phase with butyl alcohol, the following difference becomes apparent as to the boiling points: The esters resulting from the first fraction obtained have a higher percentage of higher-boiling butyl esters than those obtained from the second fraction. Besides, when extracting exhaustively, a remarkable coagulation of the high-molecular carboxylic acids or a part thereof occurs within the organic liquid phase, especially in its limiting surface, so that this coagulated part may be separated. Strangely, such coagulation may be promoted by adding salts or certain solvents, of a hydrophobic nature, such as benzene or gasolene. Simultaneously, this separation of the two phases can be favored by such additions, as stated above.

The ratio of the single constituents is essentially important for the purification effect intended. On the one hand, the distribution of the acids of the oxidation product between the organic liquid phase and the aqueous phase is determined by the ratio of the aqueous phase to the organic liquid phase and, on the other hand, by the mixing ratio of the solvents forming the organic liquid phase to each other. When choosing as organic solvents, i. e., mixtures of tetrahydrofurane and gasolene or tetrahydrofurane and ethylene trichloride, it is possible to result in no low-molecular weight constituents being dissolved by the organic solvent, accordingly, said solvent serving only in removing the high-molecular dark-colored constituents from the aqueous phase, said phase remaining together with the dissolved low-molecular weight light-colored acids. This effect of separating the high-molecular constituents may be advantageously improved by adding salts, as stated above. In some cases the succession of the substances to be added is important.

According to our copending application Serial No. 243,001, now U. S. Patent No. 2,726,262, a certain part of the undesired high-molecular weight carboxylic acids can be precipitated and removed by filtration, by saturating the acid reaction liquid with alkaline substances, or digesting the reaction product with comparatively large amounts of water. This method may be readily combined with the present by treating the filtered aqueous liquid with organic solvents, according to this invention.

The losses of organic solvents are merely nominal. It has been found, that when working up the organic and the aqueous phases, distillates are obtained splitting themselves on their part into two phases, namely an aqueous phase saturated with organic solvents and a phase of the organic solvent saturated with water. As has been found, the solvents recovered by distillation

may be immediately employed again after their separation so that the process proceeds without losses of organic solvents.

When working up with cyclohexanone according to our process, a complete removal of the nitric acid is not absolutely necessary, since cyclohexanone does not yield undesired by-products. Some adipinic acid may be formed as a product formed in itself also when oxidizing coal with nitric acid.

Without limiting the present invention to any particular procedure, the following examples are given to illustrate preferred modes of operation. Parts are given by weight.

Example I

100 parts of a crude oxidation product obtained by treating pit coal with nitric acid at elevated temperature and distilling off the residual nitric acid are stirred with 200 parts of cyclohexanone heated to about 30° C. Subsequently the mixture is thrice extracted with 400 parts of water each. The aqueous extracts containing small amounts of cyclohexanone are assembled, evaporated to 200 parts whereby cyclohexanone is recovered, and then twice extracted with 100 parts of benzene each in order to remove the nitrophenols. The aqueous solution is evaporated. The residue, 50 parts of a light-yellow product, contains, according to the starting material and the operating conditions chosen, substantially the following organic acids in varying proportions: pyromellitic acid, hemimellitic acid, trimellitic acid, mellophanic acid, benzene pentacarboxylic acid, phthalic acid, and succinic acid.

After evaporating the cyclohexanone employed by means of water vapor the residue is treated again with nitric acid, yielding, after having been subjected once again to the present process, an additional 10 parts of a light-brown product containing substantially the aforesaid acids.

Example II

700 parts of an aqueous acid solution obtained by oxidizing 100 parts of pit coal with nitric acid at elevated temperature are extracted with 200 parts of methyl cyclohexanone. The methyl cyclohexanone extract is twice agitated with 200 parts of water each. The aqueous solutions are assembled and, together with the starting solution treated with methyl cyclohexanone, evaporated to 500 parts and subsequently extracted with benzene according to Example I in order to remove nitrophenols. After evaporating the solution freed of nitrophenols, 52 parts of a light-yellow product are obtained, showing the same composition as the final product obtained according to Example I.

The methyl cyclohexanone solution is evaporated and the residue returned to the nitric acid oxidation stage.

Example III

100 parts of an oxidation product obtained by oxidizing treatment of pit coal with nitric acid and distilling off the nitric acid excess, said oxidation product containing nitrophenol, are agitated with 200 parts of butanone heated to about 30° C. 100 parts of gasolene are added to the mixture obtained. Subsequently the mixture is thrice extracted with water, firstly with 1000 parts and subsequently twice with 300 parts each. The assembled extracts are evaporated, yielding 57 parts of a light-yellow product containing only traces of nitrophenol. The butanone is distilled off and the residue freed from picric acid returned to the oxidation stage.

Example IV

100 parts of a crude oxidation product obtained by treating pit coal with nitric acid and distilling off the nitric acid excess are digested with 500 parts of water and the insoluble matter is separated. The filtrate is extracted with 100 parts of cyclohexanol and the organic liquid phase washed out with 500 parts of water. The assembled aqueous solutions and the cyclohexanol extract are separately evaporated. The residue obtained from the aqueous phase yields 50 parts of a light-yellow product. The residue resulting from the organic liquid phase is treated again with nitric acid and worked up, according to Example I.

Example V

1000 parts of an alkaline reaction liquid obtained by treating 100 parts of bituminous coal suspended in aqueous sodium hydroxide with oxygen under superatmospheric pressure and at elevated temperature are mixed with sulfuric acid so that 1 mol H_2SO_4 is employed for 1 mol of the Na(OH) employed, whereupon the liquid is thrice extracted with 200 parts of cyclohexanone each. The assembled cyclohexanone extracts are extracted thrice with 600 parts of water each. The aqueous extracts are evaporated together and the residue is sublimated, yielding 20 parts of a mixture of white-colored carboxylic acids.

Example VI

1000 parts of an aqueous solution obtained by oxidizing treatment of de-ashed coal with nitric acid, said solution consisting of 100 parts of coal oxidation product and 900 parts of water containing a little amount of nitric acid are first saturated with cyclohexanol and subsequently extracted with 100 parts of cyclohexanol saturated with water. When evaporating the aqueous phase, 61 parts of a light-brown powder are obtained, yielding 39 parts of white-colored carboxylic acids when sublimated.

The cyclohexanol phase yields 39 parts of a black-brownish powder.

Example VII

100 parts of a crude oxidation product obtained by oxidizing treatment of coal with nitric acid and subsequently distilling off the residual nitric acid are agitated with 200 parts of cyclohexanone heated to 30° C. The solution is twice shaken with 1000 parts of water each and the two aqueous extracts are separately evaporated. The first aqueous extract yields 36.7 and the second extract 22.7 parts of a light-yellow powder. Each extract is separately esterified with butyl alcohol, whereupon the ester mixtures are distilled in vacuo. The first extract yields 40 parts of a boiling range between 65–205° C. and 2.9 parts of a boiling range between 205–230° C.; 24 parts of a boiling range of 65–165° C. are obtained from the second extract, the degree vacuum employed being 0.1 mm. Hg.

Example VIII

1000 parts of an aqueous solution of a coal oxidation product resulting from pressure oxidation of coal by means of nitric acid, consisting of 100 parts of oxidation product and 900 parts of water are mixed with 200 parts of tetrahydrofurane whereupon 75 parts of gasolene (boiling range 60–100° C.) are added. Dark pasty products are precipitated; in order to complete the precipitation, 50 parts of kitchen salt are added to the agitated mixture. The organic liquid phase enriched with dark-colored constituents is formed below the aqueous phase and separated. In addition, a gasolene liquid phase containing small amounts of tetrahydrofurane is formed above the aqueous phase. The organic solvent liquid phases are separated, and the aqueous phase is extracted with methyl-ethyl ketone (butanone), the extract so obtained leaving an evaporating residue consisting of 45 parts of light-yellow carboxylic acids.

Example IX

100 parts of an oxidation product obtained by oxidation of coal with nitric acid under superatmospheric pressure are digested in 900 parts of water; after separating the undissolved constituents the aqueous solution is subsequently extracted with 100 parts of cyclohexanol at a temperature of 25° C. After evaporating the aqueous

phase, 62 parts of a purified product are obtained, yielding 40 parts of white-colored carboxylic acids by sublimation. The cyclohexanol extract is subjected to distillation with water vapor whereby the solvent is removed, leaving 23 parts of a dark-colored residue which is returned to the oxidation process together with the insoluble matter obtained by digesting with water.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A process of separating monocyclic aromatic polycarboxylic acids from a crude oxidation product resulting from a thermal oxidation of carbonaceous matter containing monocyclic aromatic polycarboxylic acids and also containing dark colored high molecular weight polycarboxylic acids, comprising the steps of subjecting said crude oxidation product to an extraction treatment with at least one polar organic solvent for both said monocyclic aromatic and said high molecular weight polycarboxylic acids so as to cause dissolution therein of said polycarboxylic acids; treating the thus formed solution of said monocyclic aromatic and high molecular weight polycarboxylic acids in said polar organic solvent with water, thus causing dissolution of said monocyclic aromatic polycarboxylic acids in said water, said high molecular weight polycarboxylic acids not being dissolved in said water, thereby forming a mixture including an aqueous solution of said monocyclic aromatic polycarboxylic acids; separating said aqueous solution of said monocyclic aromatic polycarboxylic acids from the remainder of said mixture; and recovering from said separated aqueous solution substantially pure monocyclic aromatic polycarboxylic acids.

2. A process of separating monocyclic aromatic polycarboxylic acids from a crude oxidation product resulting from a thermal oxidation of carbonaceous matter containing monocyclic aromatic polycarboxylic acids and also containing dark colored high molecular weight polycarboxylic acids, comprising the steps of subjecting said crude oxidation product to an extraction treatment with at least one water-immiscible polar organic solvent for both said monocyclic aromatic and said high molecular weight polycarboxylic acids so as to cause dissolution therein of said polycarboxylic acids; treating the thus formed solution of said monocyclic aromatic and high molecular weight polycarboxylic acids in said polar organic solvent with water, thus causing dissolution of said monocyclic aromatic polycarboxylic acids in said water, said high molecular weight polycarboxylic acids not being dissolved in said water, thereby forming a mixture including an aqueous solution of said monocyclic aromatic polycarboxylic acids; separating said aqueous solution of said monocyclic aromatic polycarboxylic acids from the remainder of said mixture; and recovering from said separated aqueous solution substantially pure monocyclic aromatic polycarboxylic acids.

3. A process of separating monocyclic aromatic polycarboxylic acids from a crude oxidation product resulting from a thermal oxidation of carbonaceous matter containing monocyclic aromatic polycarboxylic acids and also containing dark colored high molecular weight polycarboxylic acids, comprising the steps of subjecting said crude oxidation product to an extraction treatment with at least one water-miscible polar organic solvent for both said monocyclic aromatic and said high molecular weight polycarboxylic acids so as to cause dissolution therein of said polycarboxylic acids; adding to the thus formed solution of said monocyclic aromatic and high molecular weight polycarboxylic acids in said polar organic solvent at least one substance adapted to annihilate the water-miscibility of said polar organic solvent, thereby making the same water-immiscible; treating said solution of said monocyclic aromatic and high molecular weight polycarboxylic acids in said polar organic solvent with water, thus causing dissolution of said monocyclic aromatic polycarboxylic acids in said water, said high molecular weight polycarboxylic acids not being dissolved in said water, thereby forming a mixture including an aqueous solution of said monocyclic aromatic polycarboxylic acids; separating said aqueous solution of said monocyclic aromatic polycarboxylic acids from the remainder of said mixture; and recovering from said separated aqueous solution substantially pure monocyclic aromatic polycarboxylic acids.

4. A process according to claim 1, including also the steps of treating said remainder of said mixture with water so as to cause dissolution in said water of monocyclic aromatic polycarboxlic acid remaining in said mixture, said high molecular weight polycarboxylic acids not being dissolved in said water, thereby forming a second mixture including a second aqueous solution of said monocyclic aromatic polycarboxylic acids; separating said second aqueous solution of said monocyclic aromatic polycarboxylic acids from the remainder of said second mixture; and recovering from said second separated aqueous solution substantially pure monocyclic aromatic polycarboxylic acids.

5. A process of separating monocyclic aromatic polycarboxylic acids from a crude oxidation product resulting from a thermal oxidation of carbonaceous matter with nitric acid containing non-oxidized carbonaceous matter, nitrophenols, monocyclic aromatic polycarboxylic acids and also containing dark colored high molecular weight polycarboxylic acids, comprising the steps of removing said non-oxidized carbonaceous matter from said crude oxidation product; extracting said nitrophenols by means of a selective solvent therefor from the thus remaining oxidation product; subjecting the thus remaining crude oxidation product to an extraction treatment with at least one polar organic solvent for both said monocyclic aromatic and said high molecular weight polycarboxylic acids so as to cause dissolution therein of said polycarboxylic acids; treating the thus formed solution of said monocyclic aromatic and high molecular weight polycarboxylic acids in said polar organic solvent with water, thus causing dissolution of said monocyclic aromatic polycarboxylic acids in said water, said high molecular weight polycarboxylic acids not being dissolved in said water, thereby forming a mixture including an aqeuous solution of said monocyclic aromatic polycarboxylic acids; separating said aqueous solution of said monocyclic aromatic polycarboxylic acids from the remainder of said mixture; and recovering from said separated aqueous solution substantially pure monocyclic aromatic polycarboxylic acids.

6. A process of separating monocyclic aromatic polycarboxylic acids from an aqueous solution of monocyclic aromatic polycarboxylic acids and dark colored high molecular weight polycarboxylic acids obtained from a thermal oxidation of carbonaceous matter, comprising the steps of mixing said aqueous solution with at least one water-immiscible polar organic solvent for both said monocyclic aromatic and said high molecular weight polycarboxylic acids so as to cause dissolution in said polar organic solvent of said high molecular weight polycarboxylic acids and of a portion of said monocyclic aromatic polycarboxylic acids, thereby forming a polar organic solution containing mainly said high molecular weight polycarboxylic acids and a first aqueous solution containing mainly said monocyclic aromatic polycarboxylic acids; separating said polar organic solution from said first aqueous solution; treating the thus separated polar organic solution containing mainly said high molecular weight polycarboxylic acids with water, thus causing dissolution in said water of the monocyclic aro-

matic polycarboxylic acids contained in said polar organic solution, said high molecular weight polycarboxylic acids not being dissolved in said water, thereby forming a mixture including a second aqueous solution of said monocyclic aromatic polycarboxylic acids; separating said second aqueous solution of said monocyclic aromatic polycarboxylic acids from the remainder of said mixture; and recovering from said first and said second aqueous solutions susbtantially pure monocyclic aromatic polycarboxylic acids.

7. A process of separating monocyclic aromatic polycarboxylic acids from an aqueous solution of monocyclic aromatic polycarboxylic acids and dark colored high molecular weight polycarboxylic acids obtained from a thermal oxidation of carbonaceous matter, comprising the steps of mixing said aqueous solution with at least one water-miscible polar organic solvent for both said monocyclic aromatic and said high molecular weight polycarboxylic acids so as to cause dissolution in said polar organic solvent of said high molecular weight polycarboxylic acids and of a portion of said monocyclic aromatic polycarboxylic acids, thereby forming a mass including water, said polar organic solvent, said monocyclic aromatic polycarboxylic acids and said high molecular weight polycarboxylic acids; adding to said mass at least one water soluble electrolyte in an amount sufficient to salt-out said polar organic solvent from said water, thereby forming a polar organic solution containing mainly said high molecular weight polycarboxylic acids and a first aqueous solution containing mainly said monocyclic aromatic polycarboxylic acids; separating said polar organic solution from said first aqueous solution; treating the thus separated polar organic solution containing mainly said high molecular weight polycarboxylic acids with water, thus causing dissolution in said water of the monocyclic aromatic polycarboxylic acids contained in said polar organic solution, said high molecular weight polycarboxylic acids not being dissolved in said water, thereby forming a mixture including a second aqueous solution of said monocyclic aromatic polycarboxylic acids; separating said second aqueous solution of said monocyclic aromatic polycarboxylic acids from the remainder of said mixture; and recovering from said first and said second aqueous solutions substantially pure monocyclic aromatic polycarboxylic acids.

8. A process according to claim 6, including the steps of mixing said first aqueous solution separated from said polar organic solution with a least one water-immiscible polar organic solvent for said monocyclic aromatic and said high molecular weight polycarboxylic acids so as to cause dissolution in said polar organic solvent of any high molecular weight polycarboxylic acids remaining in said first aqueous solution, thereby forming a second polar organic solution containing mainly high molecular weight polycarboxylic acids and a remaining first aqueous solution containing mainly said monocyclic aromatic polycarboxylic acids; separating said second polar organic solution from said remaining first aqueous solution; treating the thus separated second polar organic solution containing mainly said high molecular weight polycarboxylic acids with water, thus causing dissolution in said water of the monocyclic aromatic polycarboxylic acids contained in said polar organic solution, said high molecular weight polycarboxylic acids not being dissolved in said water, thereby forming a mixture including a second aqueous solution of said monocyclic aromatic polycarboxylic acids; separating said second aqueous solution of said monocyclic aromatic polycarboxylic acids from the remainder of said mixture; and recovering from said first remaining and said second aqueous solutions susbtantially pure monocyclic aromatic polycarboxylic acids.

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