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MANUFACTURE OF MELLITIC ACID

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Fig. 1.

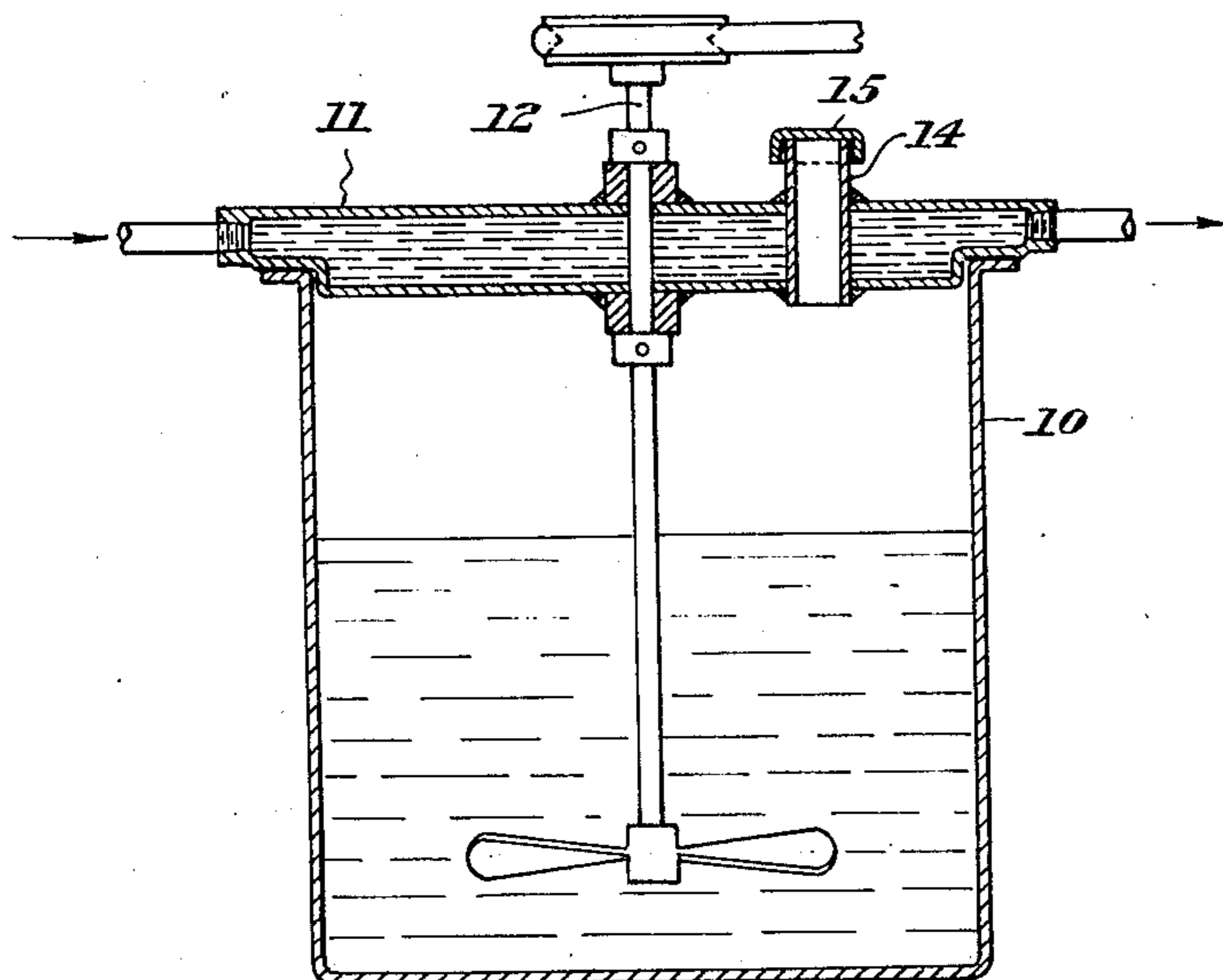
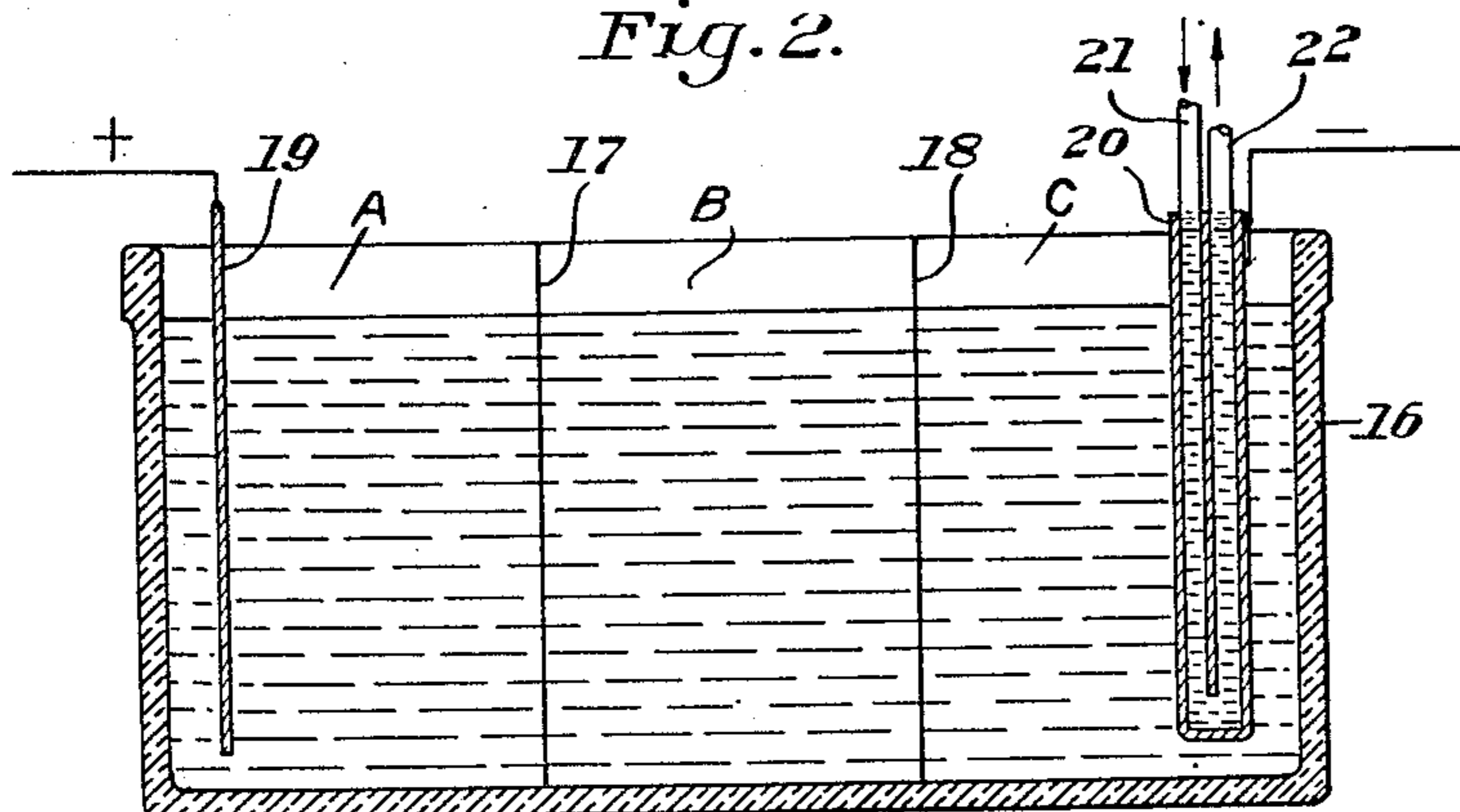


Fig. 2.



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# UNITED STATES PATENT OFFICE

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## MANUFACTURE OF MELLITIC ACID

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14 Claims. (Cl. 260—515)

My invention relates to a process for the production of mellitic acid, and more especially to a process for manufacturing mellitic acid from carbonaceous material, and has for its object to provide a simple, efficient and inexpensive method by which mellitic acid may be produced. The term "carbonaceous material" is used herein to mean coal, coke, charcoal, graphite, carbon blacks, and pitch.

Various reagents have heretofore been used by other workers to oxidize carbonaceous materials to mellitic acid, such as alkaline permanganate, sodium hypochlorite, fuming nitric acid with potassium chlorate, concentrated sulphuric acid, concentrated nitric acid, sodium chlorate and osmium tetroxide, anodic oxidation, fuming nitric acid with vanadium catalyst. The yields of the pure acid were extremely small and in most cases only crude products were obtained. The best yields were reported by H. Meyer and coworkers who oxidized carbonaceous material from various sources by refluxing with fuming nitric acid and 0.2% vanadic acid. The crude mellitic acid was converted into the ammonium salt and purified through the copper salt. Their yields are based on the crude ammonium salt. The yield of the pure acid is not given, but from experiments I have conducted following their procedure, I am forced to conclude that the yields were small. I have also found that their procedure using only fuming nitric acid and vanadium catalyst even for a prolonged oxidation period of two weeks was wholly ineffective with high temperature cokes from various coals. The oxidation stopped at the formation of high molecular intermediate compounds.

I am aware also that attempts have been made to oxidize carbonaceous material by the use of alkaline permanganate oxidation. This procedure resulted mainly in oxalic acid being formed with very little mellitic acid, when low temperature cokes were employed as the starting material. When high temperature cokes were employed as the starting material, it was found that alkaline permanganate had extremely little effect.

I have found that a very satisfactory yield of mellitic acid may be obtained from carbonaceous material by first treating the material for a suitable period of time with a suitable oxidizing acid, with or without the presence of a catalyst, followed by oxidation with an oxidizing salt such as alkaline permanganate. Mellitic acid obtained by following my method is pure, of excellent quality, and the yield is high.

The principal object of my invention is to provide a process by which carbonaceous ma-

terial may be treated to produce mellitic acid of a high quality and with a good yield. In general, my process consists of refluxing a carbonaceous material with an excess of an oxidizing acid such as fuming nitric acid, with or without the presence of a catalyst such as vanadic acid. After prolonged boiling, say, for a period of two weeks, the whole mixture is evaporated to dryness and the residue then oxidized by boiling for a considerable period of time, say one week, with an excess of an oxidizing salt, in an alkaline solution such as alkaline permanganate, and then filtering. A high yield of mellitic acid of excellent quality may be recovered from the filtrate.

With high temperature cokes and especially graphite, the superiority of the nitric acid-alkaline permanganate oxidation is best illustrated. After boiling Acheson graphite (-200 mesh) with fuming nitric acid and ammonium vanadate for two weeks, no visible change had taken place. The material had still the appearance of graphite. But on subsequent treatment with alkaline permanganate, the graphite was oxidized to mellitic acid. Graphite not pre-oxidized with nitric acid was not perceptibly attacked by alkaline permanganate.

The new procedure using fuming nitric acid and ammonium vanadate was applied to 700° C. and 1000° C. cokes. Here the nitric acid oxidation proceeded much further than with graphite and intermediate compounds were formed which, on subsequent alkaline permanganate oxidation, yielded mellitic acid. In all cases, a complete conversion of the carbon to CO<sub>2</sub>, mellitic acid and acids forming soluble ammonium salts was effected. The 1000° C. coke produced almost exclusively CO<sub>2</sub> and mellitic acid while the 700° C. coke produced CO<sub>2</sub>, mellitic acid, and acids forming soluble ammonium salts. In no case was graphitic acid, nor any other intermediate oxidation product of larger molecular size than mellitic acid, found in the final product.

*Yields of mellitic acid by the treatment with nitric acid and a catalyst followed by treatment with an oxidizing salt—per 100 gram material*

	Total acids after electrolysis	Ammonium mellitate	Mellitic acid recovered by electrolysis
	Grams		
700° C. Edenborn coke...	39.7	37.9	24.1
1000° C. Edenborn coke.	29.4	35.4	22.5
Acheson electrode graphite.....	23.7	30.0	19.1



The mellitic acid was identified by analysis and by preparing the neutral methyl ester.

In the practice of my invention, the apparatus illustrated in the accompanying drawing may be employed. In the drawing:

Figure 1 is a diagrammatic side elevation of a vessel suitable for use in boiling certain mixtures; and

Figure 2 is a diagrammatic side elevation of a three-compartment cell suitable for use in this process.

In Figure 1 of the drawing, there is shown an apparatus which can be conveniently used for boiling the mixture during a certain phase of the process. The apparatus consists of an iron vessel 10 with a removable water-cooled lid 11, through which lid a shaft 12 with a paddle adjacent the bottom of the vessel passes. This stirring device is driven by a suitable prime mover, not shown. A tube 14 passes through the cover 11, and a cover 15 is fitted over the outer end of the tube. Through this tube materials may be introduced into the iron vessel from time to time.

Figure 2 represents a three-compartment cell comprising a vessel 16 of non-conducting material divided into three cells by porous membranes 17, 18, preferably made of parchment. In compartment A, a platinum anode 19 is placed. This is called the "anodic" compartment. This compartment may be provided with a cooling coil of non-conducting material such as glass which will not affect or be affected by the liquid in the anodic compartment. In compartment C, a hollow cathode 20, formed from copper and having pipes 21 and 22 through which cooling water is circulated, is placed. This compartment is known as the "cathodic" compartment. The anode and the cathode are connected to a suitable source of direct current electricity. The compartment B is referred to as the "middle" compartment. This apparatus is more particularly described and claimed in the copending application of Henry C. Howard, Ser. No. 135,038 filed April 5, 1937. The following examples illustrate the invention.

#### Example I

Coke was formed by heating Edenborn coal to approximately 1000° C. One hundred grams of the coke (-200 mesh), together with 1500 cc. fuming nitric acid (sp. gr. 1.5) to which 0.24 gram ammonium vanadate was added, were refluxed for 14 days in an ordinary Pyrex flask with a reflux condenser. Then the whole was evaporated to dryness in a steam bath under a vacuum of approximately 20 mm. of mercury. The solid residue was dissolved in about 3 liters of water containing 200 grams of potassium hydroxide and transferred to an iron vessel provided with a double-walled, water-cooled lid with an efficient stirrer in the vessel (see Figure 1). The solution was brought to a boil and sufficient excess potassium permanganate was introduced from time to time so that the color remained purple during the seven days of boiling. During that time, less than 50 grams of potassium permanganate was used. The excess potassium permanganate was destroyed with formic acid. The manganese dioxide was filtered off and thoroughly washed. The filtrate was concentrated and placed in the middle cell of a three-compartment cell with parchment membranes separating the three-compartment cell (see Figure 2). The anodic and cathodic compartments were

filled with distilled water. To obtain good conduction, about 50 cc. formic acid was added to the alkaline filtrate. After electrolysis for four days with a current not exceeding 4 amp. at 110 volts, the acids were found to have migrated to the anode compartment. The cathodic and anodic compartments were emptied and refilled with distilled water twice during each 24 hours of the electrolysis. The combined anodic solutions were evaporated to about 300 cc. and the mellitic acid was precipitated as the ammonium salt by adding the concentrated anodic solution to 1500 cc. of a well cooled solution of ammonium hydroxide (sp. gr. 0.9). An insoluble precipitate was formed which was found to be pure ammonium mellitate free from oxalic acid or any other impurities.

The yield of the dried salt was 35.4 grams. After drying for 48 hours over sulphuric acid under a vacuum of about 20 mm. of mercury, the salt had the approximate composition of a hexahydrate. To obtain the free acid, the ammonium mellitate was added to 1000 cc. of distilled water containing 50 grams of potassium hydroxide and 12 cc. formic acid. The mixture was electrolyzed as described above. The dried residue obtained from the evaporated anodic solutions consisted of 22.5 grams of analytically pure mellitic acid.

#### Example II

One hundred grams of triphenylene (9-10 benzophenanthrene) was added to 1½ liters of nitric acid (sp. gr. 1.5) and refluxed for a period of two weeks. The whole was then evaporated to dryness over a steam bath under a vacuum of about 20 mm. of mercury. To the residue, 200 grams of potassium hydroxide dissolved in 3 liters of water was added and the mixture boiled with constant stirring for one week in an iron vessel having a water-cooled lid and an agitator in the vessel (see Figure 1). From time to time during the week, 800 grams of potassium permanganate was added at a rate such that the liquid always showed a purple color. The excess of potassium permanganate was destroyed by adding sodium formate (HCOONa). The MnO<sub>2</sub> was filtered off and washed. The filtrate contained the mellitic acid as a potassium salt. The filtrate was then concentrated by evaporation at atmospheric pressure over a steam bath to a volume of about 1 liter. The filtrate was then placed in the middle compartment of a three-compartment cell with a parchment membrane separating the compartments (see Figure 2). To obtain good conduction, about 50 cc. of formic acid was added to the alkaline filtrate. The anodic and cathodic compartments were filled with distilled water. Electrolysis was conducted for 4 days with a current not exceeding 4 amps. at 110 volts. The cathodic and anodic compartments were emptied and refilled with distilled water twice during each 24 hours.

The combined anodic solutions obtained above were converted to mellitic acid through the ammonium salt as described in Example I. The yield was 67.2 grams.

#### Example III

Five hundred grams Clairton coke (-200 mesh) was refluxed for a total period of 3 weeks with 5500 cc. nitric acid (sp. gr. 1.5) and 300 cc. nitric acid (sp. gr. 1.6). The nitric acid was added in portions. First 3000 cc. nitric acid (sp. gr. 1.5) was added. After boiling for a little more than a week, the volume of the nitric acid had de-



creased very much, but the color of the mixture was still the initial black. Then 300 cc. of nitric acid (sp. gr. 1.6) was added and boiling continued for 3 days more. The color still remained black.

5 An attempt was made to filter off the insolubles. This, however, did not work due to the colloidal nature of the reaction products. Therefore, the oxidation was continued by adding, first 2000 cc. of nitric acid (sp. gr. 1.5) and later 500 cc. of

10 nitric acid (sp. gr. 1.5). After about a week of further refluxing, the color had changed from black to light brown. It was allowed to cool and the insolubles were separated by sedimentation and filtration. In this case filtration was

15 not difficult. The insolubles were then dried and further oxidized with alkaline potassium permanganate. Less than 100 grams of potassium permanganate were used during 6 days. The excess potassium permanganate was destroyed with formic acid. The manganese dioxide was filtered off and washed. The filtrate contained the mellitic acid as a potassium salt. The filtrate was treated as was the filtrate in Example I. The yield of mellitic acid was 71.4 grams.

#### Example IV

One thousand grams of 200 mesh Fairmont coke was oxidized with 3 liters of nitric acid (sp. gr. 1.5) and 0.5 gram vanadic acid as catalyst at a temperature between 60–70° C. for one week. The mixture was then cooled and the insolubles were filtered off. The insolubles were dried and then added to 15 liters of water containing 500 grams of potassium hydroxide. The mixture was

35 placed in an iron vessel provided with a double-walled water-cooled lid and with a stirrer reaching into the vessel, as described in the previous examples. After the solution was brought to boil, 11,000 grams of solid potassium permanganate was added within 3 days. After that time the color was discharged. The manganese dioxide was filtered off and the mellitic acid recovered as in the previous examples. The yield was 150 grams.

45 It is possible to recover the mellitic acid from the alkaline filtrate as obtained, for instance, in Example I, through the barium or calcium salt. The alkaline filtrate is made just slightly acidic, for instance with hydrochloric or nitric or acetic acid, and treated with a soluble barium or calcium salt. The insoluble barium or calcium mellitate is formed. This is filtered off and treated with a sufficient amount of dilute sulphuric acid and the insoluble barium or calcium sulphates, separated by filtration, and the mellitic acid recovered by evaporation of the filtrate.

50 It is also possible to recover the mellitic acid from the alkaline filtrate as the neutral methyl ester. The alkaline filtrate is evaporated to dryness and treated with an excess of dimethyl sulphate at room temperature for several days. In this manner, the neutral methyl ester of mellitic acid is formed and the alkali hydroxide is changed to a sulphate. The inorganic matter

65 from the coke, mainly silica, is also present in this mixture. To obtain the ester, the whole mixture is treated with water and the excess dimethyl sulphate is decomposed by adding a bicarbonate. The insoluble material consisting of silica and ester is filtered off and the ester is obtained by extraction with alcohol or acetone. The ester may be purified by recrystallization from a mixture of methyl alcohol and water.

75 Instead of using dimethyl sulphate for preparing the ester, a mixture of methyl alcohol and sul-

phuric acid may be employed. The well dried evaporation residue from the alkaline filtrate is suspended in a definite volume of methyl alcohol and to this is added carefully about half that volume of concentrated sulphuric acid containing

5 copper sulphate as catalyst. After heating the mixture for one hour at 125° C., it is poured into water when silica and ester separate. The ester is obtained by extraction as above.

10 In this method the inconvenient and lengthy operation of decomposing the excess dimethyl sulphate is avoided.

15 The following table shows the yields in grams of mellitic acid per 100 grams of the following materials (pulverized to approximately –200 mesh):

	Heated at—			
	Room temp.	500° C.	700° C.	1000° C.
Pittsburgh coal.....	5.5	11.9	24.1	22.5
Illinois No. 6 coal.....	4.3	-----	-----	19.4
High splint coal.....	5.0	-----	-----	20.8
Pocahontas #3 coal.....	10.9	-----	-----	22.1
Anthracite.....	17.7	-----	-----	19.8
Cellulose (cotton).....	-----	-----	-----	24.8
Acheson graphite.....	19.1	-----	-----	-----
Natural graphite.....	21.7	-----	-----	-----
Activated charcoal.....	19.7	-----	-----	-----
Pitch from low-temperature tar.....	4.1	-----	22.9	-----
9-10-benzophenanthrene.....	67.2	-----	-----	-----
Petroleum coke.....	20.7	-----	-----	-----

20 The effect of heat treating the carbonaceous material before subjecting it to the process which I have invented is shown in the above table.

25 It may or may not be desirable to use a catalyst depending upon the conditions of the oxidation. If a large excess of nitric acid is used, the catalyst is of no advantage. If the amount of nitric acid is greatly reduced, the catalyst may be of importance by speeding up the oxidation with nitric acid. However, the yields of mellitic acid are the same whether a catalyst is used or not. But the amount of permanganate required in the second stage may be reduced by using a catalyst in the first stage, if the nitric acid is not present in large excess. I have also determined that the temperature to which the carbonaceous material is subjected before treatment has an effect on the yield of mellitic acid.

30 For example, I have found that in general better results are obtained if the coke is formed at a temperature of not less than 700° C. I have also determined that if the time of treatment with nitric acid is increased, the amount of potassium permanganate needed will be decreased. The most economical process must be ascertained experimentally for each type of carbonaceous material. These data can be readily obtained following the teachings of my invention.

35 It is evident that by the process which I have invented, mellitic acid can be produced in any desirable quantities in an economical and expeditious manner.

40 While I have specifically described the preferred embodiment of my invention, it is to be understood that the invention may be otherwise practiced within the scope of the following claims.

I claim:

70 1. In the process of making mellitic acid, the steps which consist of treating a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch with nitric acid and vanadic acid followed by a

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treatment with an alkali metal permanganate in an alkaline solution.

2. In the process of making mellitic acid, the steps which consist of treating a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch with nitric acid and a catalyzer followed by a treatment with an alkali metal permanganate in an alkaline solution.

3. In the process of making mellitic acid from a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch, the steps which consist of heating the material, refluxing the material with an excess of an oxidizing acid, evaporating the mixture to dryness, dissolving the residue in an aqueous solution of a metallic hydroxide, boiling the solution with an excess of an alkali metal permanganate, filtering the mixture, separating the acids, and recovering the mellitic acid through the ammonium salt.

4. In the process of making mellitic acid from a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch, the steps which consist of heating the material, refluxing the material with an excess of an oxidizing acid, evaporating the mixture to dryness, dissolving the residue in an aqueous solution of potassium hydroxide, boiling the solution with an excess of potassium permanganate, filtering the mixture, separating the acids, and recovering the mellitic acid through the ammonium salt.

5. In the process of making mellitic acid from a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch, the steps which consist of heating the material, refluxing the material with an excess of an oxidizing acid, evaporating the mixture to dryness, dissolving the residue in an aqueous solution of a metallic hydroxide, boiling the solution with an excess of an alkali metal permanganate, filtering the mixture, and recovering the mellitic acid through the barium salt.

6. In the process of making mellitic acid from a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch, the steps which consist of heating the material, refluxing the material with an excess of an oxidizing acid, evaporating the mixture to dryness, dissolving the residue in an aqueous solution of a metallic hydroxide, boiling the solution with an excess of an alkali metal permanganate in an alkaline medium, filtering the mixture, and recovering the mellitic acid through the calcium salt.

7. In the process of making mellitic acid from a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch, the steps which consist of heating the material, refluxing the material with an excess of an oxidizing acid, evaporating the mixture to dryness, dissolving the residue in an aqueous solution of a metallic hydroxide, boiling the solution with an excess of an alkali metal permanganate, filtering the mixture, and recovering the mellitic acid through neutral methyl ester.

8. In the process of making mellitic acid, the steps which consist of treating a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch with nitric acid followed by a treatment with potassium permanganate in an alkaline solution of potassium hydroxide.

9. In the process of making mellitic acid from a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch, the steps which consist of refluxing the material with an excess of an oxidizing acid, evaporating the mixture to dryness, dissolving the residue in an aqueous solution of a metallic hydroxide, boiling the solution with an excess of an oxidizing salt in an alkaline medium, destroying the excess of the oxidizing salt with an organic acid, filtering the mixture, concentrating the filtrate, placing the filtrate in the middle compartment of a three-compartment cell, the compartment being separated by a permeable neutral membrane, passing a current of electricity through the cell, collecting the anodic solution and evaporating it to a reduced bulk, adding the reduced bulk to a solution of ammonium hydroxide, adding the precipitate to water, electrolyzing the mixture in a three-compartment cell as above and drying the residue.

10. In the process of making mellitic acid by treating a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks and pitch, with an oxidizing acid, the step of treating the substance thus formed with a solution of an alkali metal permanganate and an alkali metal hydroxide.

11. In the process of making mellitic acid by treating a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch with fuming nitric acid, the step of treating the substance thus formed with an alkali metal permanganate in an alkaline solution.

12. In the process of making mellitic acid by treating a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch with nitric acid, the step of treating the insoluble residue thus formed with a solution of an alkali metal hydroxide and an alkali metal permanganate.

13. In the process of making mellitic acid by treating a material selected from the group consisting of coal, coke, charcoal, graphite, carbon black, and pitch by an oxidizing acid, the steps of drying the residue and then treating the residue with a solution of an alkali metal hydroxide and an alkali meal permanganate.

14. In the process of making mellitic acid from a material selected from the group consisting of coal, coke, charcoal, graphite, carbon blacks, and pitch, the steps comprising heating the material with nitric acid, filtering the insolubles, drying the insolubles and then treating the insolubles with a solution of an alkali metal hydroxide and an alkali metal permanganate.

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