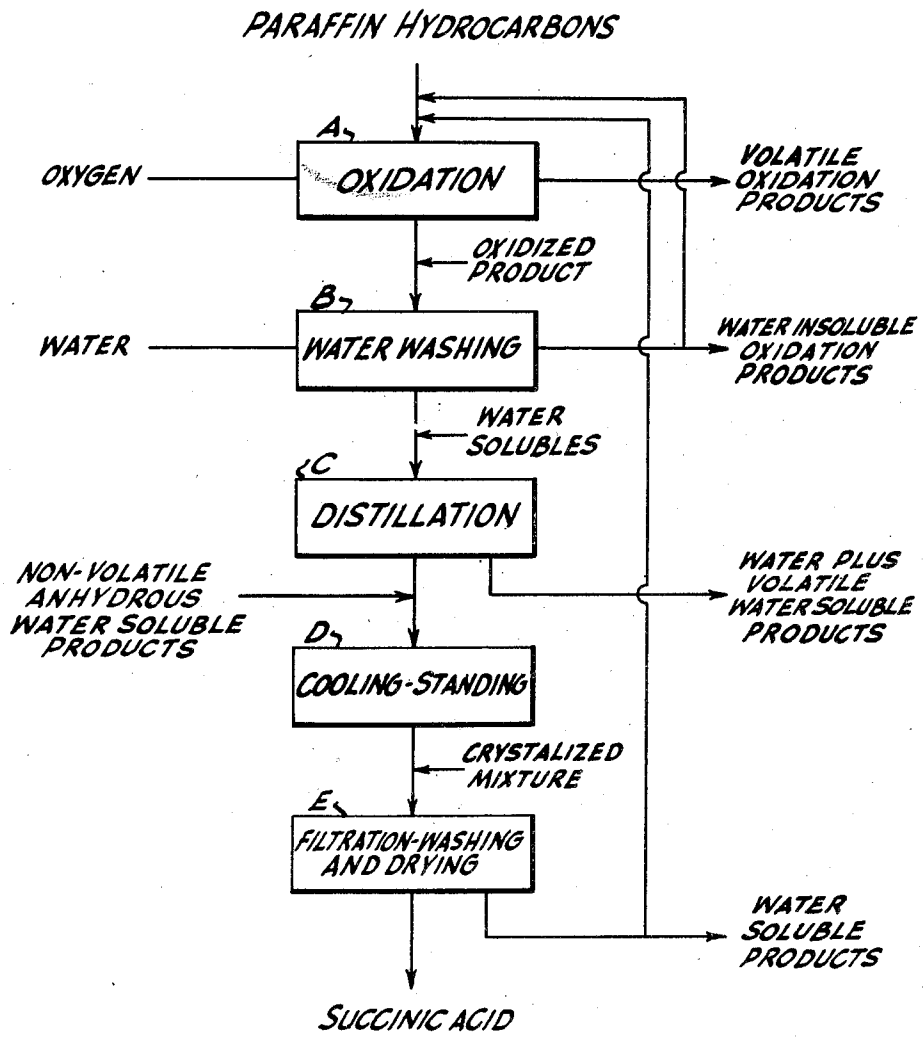
Dec. 12, 1950 O. L. POLLY 2,533,620

PRODUCTION OF SUCCINIC ACID

Filed May 24, 1948



INVENTOR.
ORVILLE L. POLLY
BY
Ross J. Garofalo

Patented Dec. 12, 1950 2,533,620

UNITED STATES PATENT OFFICE

2,533,620

PRODUCTION OF SUCCINIC ACID

Orville L. Polly, Long Beach, Calif., assignor to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Application May 24, 1948, Serial No. 28,950

5 Claims. (Cl. 260—451)

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This invention relates to the production of succinic acid and succinic anhydride by the oxidation of petroleum hydrocarbons and by the oxidation of oxidized derivatives of petroleum hydrocarbons. More particularly, this invention relates to methods for the oxidation of petroleum wax and other paraffin hydrocarbons whereby succinic acid and genitors of succinic acid are produced, to methods for the conversion of succinic acid genitors to succinic acid and to methods for the separation of succinic acid from oxidized hydrocarbon fractions.

It is thus a primary object of this invention to provide a method for the synthesis of succinic acid from paraffin wax and/or other paraffinic hydrocarbons.

It is another object of this invention to provide a method for the synthesis of succinic acid from oxidation products of paraffinic hydrocarbons, such as fatty acids.

It is another object of this invention to provide a process for the separation of succinic acid from mixtures of oxidized paraffinic substances.

Briefly, my invention involves the synthesis of succinic acid and genitors of succinic acid by the oxidation of selected paraffin wax fractions. The petroleum wax fraction is oxidized by blowing the melted wax with an oxygen-containing gas at moderate temperatures until a relatively high acid number has been obtained. In the preferred modification of my invention, the succinic acid precursors are converted to succinic acid by the action of boiling water and together with the succinic acid already present are simultaneously extracted from the oxidized wax along with the other water-soluble constituents by the action of the boiling water. The hot, aqueous extract containing the succinic acid is then distilled, preferably under vacuum, to remove the more volatile acids and the water. The succinic acid-containing residue from the distillation is cooled and allowed to stand, whereupon solid succinic acid is crystallized therefrom and removed by filtration.

The process of the present invention, which includes the individual operations of the combined oxidation and separation method for the production of succinic acid, may be more clearly understood by reference to the accompanying diagram which is a schematic diagram of the overall process of the oxidation and separation, and depicts the individual steps of the process.

Referring particularly to the diagram, the preferred oxidation feed stock to step A is a petroleum paraffin wax which is predominantly

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composed of paraffinic hydrocarbons having between about 15 and 50 carbon atoms per molecule, and more preferably between about 20 and 35 carbon atoms per molecule. The wax is preferably a higher melting wax such as those refined waxes which melt at about 90° F. and preferably above 120° F.

The wax should be substantially free of any hydrocarbons containing aromatic rings since these compounds will oxidize to form inhibitors which repress further oxidation of the residual hydrocarbons. The wax to be oxidized should also be relatively free of hydrocarbons containing naphthene rings since these tend to form peroxides in the product which, in some cases, seem to decrease the yield of desirable oxidation products.

A very suitable wax for the production of succinic acid is one which has been prepared by modern solvent refining technique. Thus, a topped petroleum residuum or lubricating oil fraction thereof is extracted with liquefied propane to separate asphalt from the oil and the thus de-asphalted oil in propane solution is subsequently de-waxed by chilling to temperatures in the neighborhood of —40° F. to crystallize wax which is then separated, such as by filtration, settling or centrifuging, from the propane-oil solution. The thus separated wax from the de-waxing step contains oil and this oil is removed by chilling it and then adding a cold solvent, such as methyl ethyl ketone, to dissolve oil and low melting wax and then filtering to separate a high melting de-oiled wax. Such methods are well known and are generally described in U. S. Patent No. 2,229,658. The wax thus obtained by this and other solvent refining processes is relatively free of objectionable materials for wax oxidation purposes. The melting point of the refined wax is usually above 90° F. and may even be as high as 165° F. or more. Such waxes are substantially straight chain normal paraffins and are only slightly isoparaffinic. Although solvent refining gives a very desirable oxidation feed stock, waxes refined by other methods and from other sources may also be used in the process of this invention, such as refined tank bottoms wax and other petroleum-derived wax fractions.

Although the paraffin waxes are the most desirable feed stocks for the production of succinic acid, other hydrocarbons such as paraffins and isoparaffins, which contain at least 10 carbon atoms per molecule, may also be employed provided they comprise mostly molecules which con-

tain an unsubstituted tetramethylene grouping of the type illustrated by the following formula:

$$R—CH_2—CH_2—CH_2—CH_2—R'$$

wherein R and R' are saturated aliphatic radicals which contain at least 3 carbon atoms.

The oxidation of the paraffin wax in step A is carried out in the liquid phase by blowing the melted wax with an oxygen-containing gas until the desired acid number has been attained. The yield of succinic acid and genitors of succinic acid obtained by the oxidation of wax is dependent upon the temperature of the oxidation. High temperatures promote the decomposition of succinic acid and/or its derivatives and at lower temperatures the oxidation reaction is unduly slow. The oxidation is carried out at a temperature above the melting point of the wax and below 160° C., or between about 100 and 160° C. The preferred temperature range is from 120 to 140° C.

The oxidation of the paraffin wax is continued until the acid number is between about 200 and 250 and preferably in the range of 235 to 250. When the oxidation is discontinued at acid numbers below 200, little or no succinic acid is obtained. When the oxidation is continued until the acid number is in the range of 235 to 250, the greatest yield of succinic acid is obtained and also the succinic acid is more readily separated from such oxidized products according to the methods of this invention.

The term "acid number" represents the numerical value of the "acidity" which latter term has the units of mg. of KOH per gram. The method for the determination of acid numbers is described in "A. S. T. M. Standard on Petroleum Products and Lubricants," October 1947, page 639.

In step A, the oxidation feed stock is subjected to liquid phase oxidation by contacting the melted feed stock with a gas containing free oxygen, such as air, oxygen-enriched air, oxygen and the like. The oxidation is preferably carried out under pressures which may vary between 1/10 and 20 atmospheres and preferably between normal atmospheric pressure and 10 atmospheres. The oxidation temperature is above the melting point of the wax being oxidized and below 160° C. and is preferably in the range of 120 to 140° C. The wax is melted and introduced into a reaction vessel which is equipped with means for both heating and cooling the contents. The vessel is preferably in the form of a vertical column provided with heating coils in the lower section, and is only partially filled with the molten wax in order to leave ample free space above the liquid to provide for foaming and vapor space. The melted wax is then heated to between about 100 and 160° C. by means of the heating coils and the gas containing free oxygen, such as air, is passed into the bottom of the vessel under pressure through a distributor which insures adequate dispersion of the air in the form of fine bubbles throughout the liquid. This insures efficient air utilization in the oxidation. The volumetric rate at which the air or other oxidizing gas is introduced may vary between about 1 and 20 cubic feet per barrel of hydrocarbon per minute. The barrel herein referred to is the 42-gallon barrel of the petroleum industry. The preferred air rate is between about 10 to 15 cubic feet per barrel per minute. The oxidation is performed under pressure which increases the oxidation rate and also limits excessive evaporation of the desired oxidation products, while allowing the evaporation of some of the lower molecular weight acidic oxidation products. The effect of oxidizing under pressure only increases the reaction rate and does not alter the product distribution or types of products providing the pressure is in the range of 1/10 to 20 atmospheres. The volatilized lower molecular weight compounds may be subsequently recovered and purified according to conventional processes. The removal of the lower molecular weight acids appears to aid the oxidation. The effluent gases leaving the oxidizing vessel may be cooled so as to recover the lower molecular weight normally-liquid oxidation products. These products include formic, acetic, and propionic acids and other oxygenated materials.

The oxidation operation, above described as a batch process conducted in a single vessel, may be conducted on a continuous basis in a series of smaller vertical reaction vessels, each equipped for heating and cooling and provided with means for introduction of the gas containing oxygen. The paraffin wax may be passed successively through the series of vessels to undergo oxidation. The advantages offered by such a mode of operation include, among others, a steady flow of product, a uniform product quality, and the ease of control of the operation.

Following the initiation of the oxidation reaction, less heat is required to maintain the desired temperature because of the heat developed by the reaction. Thus, it is sometimes necessary to discontinue heating and remove heat by cooling the reactor to maintain the desired temperature. Whether the operation is carried out exothermically or endothermically is largely determined by the pressure of the operation, temperature, and the amount of air or other oxygen-containing gas employed in the reaction as well as the size of the oxidation vessel.

During the oxidation step, a considerable quantity of volatile low molecular weight oxidation products are recovered by cooling and separation from the accompanying water formed by the oxidation process. A separation of these materials is relatively simple and is carried out by conventional methods.

The oxidized wax is then water washed in step B which water washing serves to convert succinic acid genitors to succinic acid and to extract the succinic acid from the oxidized wax along with the other water-soluble components such as lower molecular weight fatty acids, alpha-hydroxy acids and the like. The water washing process is most easily conducted at 50 to 130° C. and preferably at 80 to 120° C. Under these conditions, the oxidized wax is melted and the water washing operation is facilitated by the fluidity and increased mobility of the molten oxidate. When the washing is carried out at temperatures above about 100° C., it is necessary to employ a suitable pressure on the system to prevent distillation of the water from the mixture. It is generally desirable to use two or more washes employing about 2 to 10 volumes of water per volume of oxidized wax per wash. Any convenient apparatus may be used for the water washing step such as a series of mixing and settling vessels or a conventional extraction column.

The water washed, water-insoluble oxidized wax fraction generally has an acid number of about 100 to 175 when an oxidized wax having an acid number of about 250 is washed. The water-washed, oxidized wax contains oxygenated prod-

ucts which generally range from about 6 to 50 or more carbon atoms per molecule. The composition usually approximates about 45 per cent alpha-hydroxy acids and estolides, 35 per cent fatty acids, 15 per cent neutral esters, and 5 per cent by weight of unreacted wax.

The water-insoluble water washed oxidized wax may be processed to recover its valuable constituents. Alternatively however, the fraction can be recycled to the oxidizer wherein more succinic acid can be produced by its oxidation.

The aqueous extract from water washing step B is distilled in step C to remove the water and the bulk of the oxidation products which are more volatile than succinic acid. The distillation step is most easily carried out by first distilling off most of the water at atmospheric pressure whereby a product containing about 10 to 30 per cent by weight of water is obtained. The removal of the residual water and volatile oxidation products is best accomplished by a distillation at reduced pressure. Vacuum distillation permits lower temperatures to be employed which factor prevents extensive decomposition and reaction of the components of the concentrate. It is generally desirable to keep the distillation temperatures below about 220° C.

The anhydrous concentrate produced in step C is next cooled and allowed to stand undisturbed in step D at about 10 to 35° C. Crude succinic acid crystallizes from the concentrate in from 2 to 10 days. The crystallization of the succinic acid may be accelerated by seeding the concentrate with a few crystals of pure succinic acid.

The mixture of crude succinic acid crystals and the mother liquor from step D are separated in step E by any suitable method such as filtration, decantation, and the like and the separated crystals are preferably washed with a solvent to remove the adhering mother liquor. Suitable solvents which may be employed for this purpose include benzene, toluene, xylene, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, di-ethyl ketone, di-ethyl ether and the like. The excess solvent may be removed from the crude acid by evaporation in a vacuum.

The crude succinic acid obtained from step E can be purified by any well known process such as sublimation, recrystallization, and the like.

The mother liquor from step E logically should contain the higher molecular weight, less volatile, water-soluble oxidation products. However, the mother liquor is in general not completely soluble in water and it is believed that a part of the original water-soluble compounds are converted to water insoluble compounds during the distillation in step C. The mother liquor contains fatty acids, alpha-hydroxy acids and estolides, and unidentified decomposition products. This material may be recycled to the oxidation step to produce additional succinic acid or, alternatively, it may be processed to recover its component materials.

The preferred method for the separation of succinic acid from oxidized wax is the one which has just been described in detail. However, other methods may also be employed to effect this separation. The succinic acid concentrate which is produced from the distillation step C can be subjected to further distillation to distil succinic acid and/or anhydride from the mixture. The distillation is conducted at a reduced pressure such as below 150 mm., and preferably below 30 mm. At higher pressure, extensive decomposition of the succinic acid and of the remaining components of the mixture takes place as a result of the higher temperatures required. By employing pressures in the range of 0.5 to 5 mm., the succinic acid and/or anhydride are volatilized by heating the mixture to about 150 to 220° C. The succinic acid and anhydride generally crystallize out of the cooled distillate in fairly pure form. It is desirable to first distil the concentrate to separate the compounds boiling below the succinic acid and thence to distil the succinic acid and/or anhydride overhead as a separate and relatively rich fraction. A purer succinic acid is obtained thereby.

The general process which has been described in detail may be modified by mixing the anhydrous non-volatile, residue from the distillation step C with a solvent in which the succinic acid is less soluble than the remaining components. In some instances, the addition of such a solvent to the distillation residue induces more rapid and complete separation of the succinic acid from the mixture on standing. In other cases purer succinic acid is produced than would otherwise be obtained. The mixture of the residue and solvent can also be chilled to crystallize out the maximum yield of succinic acid since the added solvent reduces the usual tendency of the mixture to set to a viscous mass which, on further cooling, sets up to a glass. Suitable solvents for this purpose include diethyl ether, di-isopropyl ether, methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, diethyl ketone, propyl alcohol, and the like.

The general process for the production of succinic acid by oxidation and separation can also be carried out using raw materials other than petroleum hydrocarbons. The oxidation of the water-insoluble fraction of oxidized wax which comprises mostly fatty acids, alpha-hydroxy acids and estolides of alpha-hydroxy acids also yields succinic acid. Similarly, the oxidation of pure fatty acids containing more than about 7 carbons per molecule also yields succinic acid. Mixtures of suitable fatty acids may be obtained by the oxidation of any suitable petroleum hydrocarbons. Suitable fatty acids can also be obtained from plant and animal sources. In the oxidation of fatty acids, water-insoluble oxidized wax fractions and the like substantially the same methods and conditions of oxidization and of separation of the succinic acid from the oxidized product are employed as have been hereinbefore described for the oxidation of wax and the separation of succinic acid from the oxidized wax.

Perhaps the process of this invention can best be understood by reference to the following specific examples:

Example I

About 100 parts by weight of a refined petroleum wax having a melting point between 145 and 155° F. was introduced into an oxidation vessel provided with heating and cooling coils. The wax was melted and the temperature increased to about 130° C. Air at a pressure of 150 pounds per square inch gauge was employed as the oxidizing agent and was passed through the oxidation vessel at a rate of about 5.5 cubic feet per barrel per minute. At the end of about 24 hours, the oxidation reaction had begun to progress satisfactorily and the temperature was lowered to 120° C. At the end of 132 hours, the oxidation was stopped. About 107 parts by weight of an oxidized product having an acid number of 250 was obtained.

The 107 parts by weight of oxidized wax was melted, heated to 95° C., and washed four times with water at about 95° C., employing about 215 parts by weight of water per wash. The combined water washes comprised about 26.8 parts by weight of water-soluble oxidation products in about 860 parts by weight of water. The combined water washings were distilled at atmospheric pressure until the temperature of the still bottoms was about 145° C. A succinic acid-containing mixture was obtained as the bottoms product which contained 17.1 parts by weight of organic oxidation products and 4.3 parts by weight of water. The succinic acid-containing mixture was then heated to 150° C. under 1 mm. of pressure to evaporate the residual water and volatile oxidation whereupon a non-volatile concentrate amounting to 15.6 parts by weight was obtained. The concentrate was cooled and allowed to stand at room temperature for about three weeks. Crude succinic acid crystallized from the concentrate and was removed by filtering through a Büchner funnel. The crystals were freed of adhering mother liquor by pouring benzene through the funnel and evaporating the adhering benzene. About 3.3 parts by weight of crude succinic acid was thus obtained and was estimated to contain about 80–95 per cent by weight of succinic acid.

The crude succinic acid was partially purified by recrystallization from ethyl alcohol. The following data compare the "succinic acid from oxidized wax" with the literature data for succinic acid:

	"Succinic Acid from Oxidized Wax"	Succinic Acid, Literature Data
Melting point, ° C.	175–180	189–190
Equivalent Weight	59.5	59.05
Elemental Analysis, Wt. Per cent:		
Carbon	42.54	40.68
Hydrogen	4.72	5.12
Oxygen	52.74	54.20
Total	100.00	100.00

Example II

A sample of oxidized wax was prepared and water washed according to the method described in Example I. The four water washings were combined and distilled at atmospheric pressure until the temperature of the still bottoms was about 145° C. The succinic acid-containing mixture, which was obtained as the bottoms product, contained 17.1 parts by weight of organic oxidation products and 4.3 parts by weight of water based on 107 parts of crude oxidate taken. The mixture was then vacuum distilled at 1 mm. pressure until the temperature of the distillation flask was 150° C. The temperature of the distillation was raised to 220° C. and the distillate volatilized from the mixture between 150 and 220° C. at 1 mm. pressure was collected and cooled. Crude crystals of succinic acid and anhydride separated from the cooled distillate and, after washing on a filter with benzene and subsequently drying, amounted to about 2.5 parts by weight. The product was estimated to contain 85–95 per cent by weight of succinic acid and anhydride.

Example III

The water-insoluble fraction of the oxidized wax prepared in Example I amounted to about 80 parts by weight and had an acid number of about 170. The water-insoluble fraction contained the following components:

Component:	Per cent by weight
Alpha-hydroxy acids and estolides	45
Fatty acids	37
Neutral esters	14
Unreacted paraffin wax	4

The water-insoluble fraction was melted, returned to the oxidizer and reoxidized at a temperature of about 121° C. About 5.5 cubic feet of air per barrel of oxidizer feed per minute was employed at a pressure of 150 pounds per square inch. At the end of about 35 hours the acid number was 250. About 82 parts by weight of product were obtained. The product was water washed at 95° C. four times employing about 150 parts by weight of water per wash. The water washings were combined and distilled at atmospheric pressure until the distillation bottoms was about 145° C. The non-volatile fraction was transferred to a vacuum distillation apparatus and distilled at 1 mm. pressure until the distillation bottoms was about 150° C. A part of the residue was removed and cooled whereupon succinic acid separated therefrom. The remainder of the residue was distilled at 1 mm. pressure and the 150 to 220° C. fraction was collected and cooled, whereupon succinic acid and anhydride separated therefrom.

Example IV

Example I was repeated with the exception that pure n-hexadecane ($C_{16}H_{34}$) was employed as the oxidation feed stock in place of the petroleum wax. The oxidation was carried out at a temperature of 132° C. and the oxidation was stopped when the acid number of the oxidized material was 235. The product was water washed and the water washings were distilled, first at atmospheric pressure and then at 1 mm. pressure to remove the water and oxidized products boiling below 145° C. at 1 mm. pressure. The distillation residue was cooled and allowed to stand for about 1 week. The succinic acid crystals were separated, washed with benzene and dried. About 2.5 parts of succinic acid per 100 parts of the original n-hexadecane were obtained therefrom.

Example V

Example I was repeated with the exception that pure stearic acid was substituted for the petroleum wax as the oxidation feed stock. The oxidation was carried out at 121° C. until an acid number of 250 was attained. The product was water washed and the water washings were distilled according to the procedure described in Example I. Succinic acid crystallized from the distillation residue after cooling and standing.

The foregoing disclosure of my invention is not to be considered as limiting since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. A process for the production of succinic acid which comprises oxidizing a paraffinic hydrocarbon at a temperature between 100° C. and 160° C. by blowing with an oxygen-containing gas until the acid number of the resulting oxidizing mixture is between 200 and 250 mg. of KOH per gram, discontinuing said oxidation, water washing said oxidized mixture at a temperature between about 50° C. and 130° C. to produce a water-soluble extract, evaporating said water-soluble extract to remove water and oxidation

products more volatile than succinic acid and thereby forming an evaporated water-soluble extract, cooling said evaporated water-soluble extract and thereby causing solid succinic acid to precipitate therefrom and removing said succinic acid.

2. A process according to claim 1 wherein said paraffinic hydrocarbon is a petroleum wax having a melting point between 90° F. and 165° F.

3. A process according to claim 1 wherein said blowing with an oxygen-containing gas is conducted at a pressure between about 1 and 10 atmospheres.

4. A process for the production of succinic acid which comprises oxidizing a paraffinic hydrocarbon in an oxidation step at a temperature between 100° C. and 160° C. by blowing with an oxygen-containing gas until the acid number of the resulting oxidized mixture is between 200 and 250 mg. of KOH per gram, discontinuing said oxidation, water washing said oxidized mixture at a temperature between about 50° C. and 130° C. to produce a water-soluble extract, evaporating said water-soluble extract to remove water and oxidation products more volatile than succinic acid thereby forming an evaporated water-soluble extract, cooling said evaporated water-soluble extract thereby causing solid succinic acid to precipitate therefrom, removing said solid succinic acid from its mother liquor and recycling said mother liquor to said oxidation step.

5. A process for the production of succinic acid

which comprises oxidizing a paraffinic hydrocarbon in an oxidation step at a temperature between 100° C. and 160° C. by blowing with an oxygen-containing gas until the acid number of the resulting oxidized mixture is between 200 and 250 mg. of KOH per gram, discontinuing said oxidation, water washing said oxidized mixture at a temperature between about 50° C. and 130° C. to produce a water-soluble extract and a mixture of water-insoluble oxidation products, recycling said mixture of water-insoluble oxidation products to said oxidation step, evaporating said water-soluble extract to remove water and oxidation products more volatile than succinic acid thereby forming an evaporated water-soluble extract, cooling said evaporated water-soluble extract thereby causing solid succinic acid to precipitate therefrom and removing said succinic acid.

ORVILLE L. POLLY.

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