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(54) **Catalyst metal separation from saturated aliphatic monocarboxylic acids**

(57) A process for separating soluble copper and manganese catalysts from organic saturated monocarboxylic acids having 3 to 9 carbon atoms comprises precipitating the copper and manganese as oxalates.

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SPECIFICATION

Catalyst metal separation from saturated aliphatic monocarboxylic acids

- 5 *Background of the invention* 5
- In the production of organic saturated aliphatic monocarboxylic acids having 6 to 9 carbon atoms by oxidation of the corresponding aldehydes, soluble manganese and copper compounds, such as manganous acetate and cupric acetate, are used in combination as catalysts to provide high carbon conversion and high efficiency of aldehyde to acid. High carbon conversion and high efficiency are essential not only to provide the good yields of acids but also to produce relatively small amounts of undesirable by-products and thus avoid recycling unreacted starting materials. The oxidation reaction can be conducted in the liquid phase using a single stage or multiple stage reactors. These reactions can be operated under pressure in the range from about 60 to about 150 pounds per square inch gauge, preferably from about 85 to about 95 pounds per square inch gauge, with air or oxygen containing gas in the temperature range from about 50°C. to about 80°C. Such a process is described in copending application No. 8025936 assigned to the same assignee and filed concurrently with this application. 10 15
- However, it has been found that metallic copper will precipitate from acids prepared using such mixed soluble catalyst compounds due to reduction during the processing of these acids, especially during distillation. The presence of precipitated copper particles in turn can lead to serious mechanical problems such as reboiler fouling and erosion of pump impellers. Manganese compounds, on the other hand, tend to remain soluble and are not readily reduced to the metal. 20
- Removing the soluble metal catalysts from the acid products would not only avoid the aforementioned mechanical problems but would also provide purer acid products. As has been described in copending application No. 8025932 assigned to the same assignee and filed concurrently with this application, the copper and manganese from soluble catalysts can be precipitated from organic saturated aliphatic monocarboxylic acids having 6 to 9 carbon atoms by the addition of aqueous oxalic acid. This procedure utilizes water as a separation means for the precipitated metal oxalates, since the organic acids, being substantially insoluble in water, form a separate organic phase from the aqueous phase containing the precipitated metal oxalates. The resulting organic acids which have been rendered substantially free of manganese and copper then can be readily decanted from the aqueous phase, and need not be filtered. 25 30
- However, using aqueous oxalic acid to remove copper and manganese from lower organic saturated aliphatic monocarboxylic acids containing 2 to 5 carbon atoms is not economically feasible since these acids are soluble in water, and following the addition of the aqueous oxalic acid the resulting solution would have to be distilled to recover the desired acid products. 35
- In the prior art, there are various techniques to describe the removal of metal catalysts from the reaction product. In U.S. Patent No. 3,840,469, there is a disclosure for the cobalt catalyst recovery from an acetic acid medium derived from the liquid phase oxidation of aliphatic hydrocarbons. This procedure precipitates the cobalt as cobalt oxalate in the acetic acid product. The patent indicates that manganese would not undergo precipitation in this procedure. In U.S. Patent No. 2,380,731, a procedure is described using oxalic acid to remove numerous metals such as iron, magnesium, chromium, copper, vanadium etc. from a refractory inorganic support such as a clay or alumina or silica or an alumina-silica refractory catalytic cracking catalyst. 40
- These procedures are not related to the process of this invention.
- Summary of the invention*
- 45 The present invention provides a simple means for separating manganese and copper from organic saturated aliphatic monocarboxylic acids having 3 to 9 carbon atoms. This is accomplished by adding to organic acids containing soluble metal catalysts a sufficient amount of oxalic acid to precipitate the copper and manganese as their oxalates. The precipitated oxalates then can be separated from the organic acids by filtration or centrifugation, and preferably by continuous centrifugation. The resulting organic acids then can be purified further by distillation. 50
- The organic acids subjected to the separation process of this invention are derived from the oxidation of their corresponding aldehydes using catalytic amounts of a mixture soluble manganese and copper catalysts, such as manganous acetate and cupric acetate, which are soluble in the acid product, and will contain from 3 to 9 carbon atoms. These acids include propanoic, butanoic, pentanoic, hexanoic, heptanoic, octanoic and nonanoic acids. Water will preferably not be used when separating the precipitated metal oxalates from organic acids containing 3 to 5 carbon atoms, since these acids are soluble in water and distillation would have to be employed to separate water from acid. Organic acids containing 6 to 9 carbon atoms, however, are substantially insoluble in water, and can be purified following the addition of oxalic acid in the manner described in copending application Docket 5872. 55
- 60 The amount of oxalic acid present in the organic acids should be sufficient to precipitate most of the soluble manganese and copper catalysts from the organic acids. Preferably at least a stoichiometric amount of oxalic acid to metal catalysts should be used, and it is desirable to use an excess of oxalic acid to assure complete precipitation. For example, excesses of 2 to 1000 per cent oxalic acid can be used, if desired.
- The invention will be illustrated by the following examples.

Example 1

n-Heptanoic acid (22,982 grams) produced by the oxidation of n-heptanal in the presence of a catalyst consisting of a combination of cupric acetate and manganous acetate (300 parts per million copper and 300 parts per million manganese) was combined at ambient temperatures with 32.63 grams of oxalic acid (10% excess of oxalic acid to copper and manganese on a mole to mole basis). After stirring for 9 hours, cupric and manganous oxalates precipitate from the heptanoic acid, settled and were filtered, leaving clear substantially metal-free heptanoic acid.

Example 2

The procedure of Example 1 was followed in every respect but one, the heptanoic acid containing the oxalate precipitates centrifuged. Clear, substantially metal-free heptanoic acid was recovered.

Example 3

n-Nonanoic acid (22,826 grams) produced by the oxidation of n-nonanal in the presence of a catalyst consisting of a combination of cupric acetate and manganous acetate (300 parts per million each of copper and manganese) was combined at room temperature with 32.41 grams oxalic acid (10% excess of oxalic acid to copper and manganese) and stirred for 10 hours. Cupric and manganous oxalates, precipitated from the nonanoic acid, settled and were filtered, leaving clear substantially metal-free nonanoic acid.

In addition to the acids disclosed in the foregoing examples, copper and manganese metals can be separated from other acids such as propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, and octanoic acid.

The preferred technique of removing soluble copper and manganese catalysts from higher carbon (6-9) containing monocarboxylic acids as described and claimed in copending application Docket 5872 is described in Examples 4-6.

Examples 4-6

n-Heptanoic acid produced by the oxidation of n-heptanal in the presence of a catalyst consisting of a combination of copper acetate and manganese acetate (330 parts per million copper and 295 parts per million manganese) was combined at ambient temperatures with an excess of oxalic acid to the copper and manganese present (on a mole to mole basis). The oxalic acid was added as an aqueous solution. The volume ratio of heptanoic acid present to the water in the aqueous oxalic acid can range from 1.7/1 to 9.2/1. Two phases, an organic acid phase and an aqueous phase, form. The copper and manganese oxalates precipitate from the organic acid phase into the aqueous phase, and the precipitated oxalates subsequently settled. The time required for the organic and aqueous phases to form decreased as the organic acid to water volume ratio decreased. Table I illustrates the results utilizing an organic acid to water volume ratio of 1.7.

TABLE I

Example	Organic Product	Organic Acid: Water Volume Ratio	% Excess of Stoichiometric Amounts of Oxalic Acid to Metals	Organic Phase		Initial Phasing Time
				Copper % Removal	Mn % Removal	
4	heptanoic acid 330 ppm Cu and 295 ppm Mn	1.7	2	99.9	99.6	~3 minutes
5	heptanoic acid 330 ppm Cu and 295 ppm Mn	1.7	10	99.9	99.9	~3 minutes
6	nonanoic acid 400 ppm Cu and 360 ppm Mn	1.7	10	99.9	99.9	~2 minutes

CLAIMS

1. A process for separating manganese and copper from organic saturated aliphatic monocarboxylic acids having 3 to 9 carbon atoms which comprises treating said metal-containing organic acids with oxalic acid, in an amount sufficient to precipitate substantially all of the copper and manganese as cupric oxalate and manganous oxalate, and separating said oxalates from said acids. 5
2. A process according to claim 1 wherein said oxalates are filtered from said acids.
3. A process according to claim 1 wherein said oxalates are separated from said acids by centrifugation.
4. A process according to any of claims 1, 2 or 3 wherein said acid is heptanoic acid.
5. A process according to any of claims 1, 2 or 3 wherein said acid is nonanoic acid. 10
6. A process for separating manganese and copper from saturated aliphatic monocarboxylic acids having 3 to 9 carbon atoms substantially as hereinbefore described with reference to the examples.
7. A process for oxidising saturated aliphatic aldehydes having 3 to 9 carbon atoms to their corresponding acids using soluble copper and manganese catalysts, wherein said catalysts are separated from said acids by a process according to any of claims 1 to 6. 15
8. A process for oxidising saturated aliphatic aldehydes having 3 to 9 carbon atoms to their corresponding acids, substantially as hereinbefore described with reference to the examples.
9. A saturated aliphatic monocarboxylic acid having 3 to 9 carbon atoms prepared by a process according to claim 7 or 8.