

PATENT SPECIFICATION

800,214

Inventor :—ALFRED FRANK MILLIDGE.



Date of filing Complete Specification : Nov. 15, 1956.

Application Date : Nov. 29, 1955. No. 34095/55.

Complete Specification Published : Aug. 20, 1958.

Index at Acceptance :—Class 32, B5A.

International Classification :—B01d.

COMPLETE SPECIFICATION.

Improvements in or relating to the Distillation of Organic Acid Mixtures.

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12 Torphichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

The present invention relates to the treatment of organic acid mixtures containing formic acid, more particularly those obtained by the oxidation of organic compounds.

In operations involving the treatment of organic acids, such as distillation operations, it is necessary to use corrosion resistant materials of construction because of the highly corrosive nature of mixtures containing formic acid, acetic acid and other aliphatic acids; in particular formic acid is highly corrosive. As a result stainless steel is a usual material for the construction of apparatus to be used for such operations. Stainless steel, however, is corroded by formic acid, and investigations have been made to determine the conditions under which this corrosion will be a minimum. These investigations have shown (Lane, Golden and Acheman, Industrial & Engineering Chemistry, 1953, Volume 45, page 1067) that the corrosion of stainless steel by hot formic acid is a maximum in the presence of air and a minimum in the absence of air, and these findings have been verified by the applicants.

It is an object of the present invention to provide a process involving the heat treatment of aliphatic acids obtained by the oxidation of hydrocarbons or ketones, containing formic, acetic and other acids, in apparatus constructed at least in part of stainless steel, in which the corrosion of stainless steel is reduced to a minimum.

Accordingly the present invention is for a process for the distillation in apparatus constructed at least in part of stainless steel, of a mixture of lower aliphatic acids including a minor proportion of formic acid obtained by the oxidation with molecular oxygen of hydrocarbons or ketones in which corrosion of the stainless steel is minimised by the addition of a peroxide to the mixture.

The mixture of aqueous aliphatic acids containing a minor proportion of formic acid generally comprises an aqueous mixture of formic, acetic, propionic and butyric acids wherein the formic acid content is less than about 25% by weight of the mixture. Such acid mixtures are obtained for examples by the processes described in British Patents Nos. 743,989; 743,990 and 743,991 which relate to the production of aliphatic acids by the oxidation of lower paraffinic hydrocarbons. In such oxidations, ketones such as acetone and methyl ethyl ketone are intermediate products and accordingly ketones may serve as starting materials in the oxidation reaction to produce the mixture of aliphatic acids to be treated according to the invention. The oxidation product is usually submitted to a series of distillation steps to recover the acids, and the invention is useful with any of the acid-containing mixtures so obtained, as well as with the oxidation product itself. Even during the distillation of formic acid from higher acids, the invention may be used to reduce corrosion in at least the base of the still and the lower parts of the column.

The stainless steel employed in the construction of the apparatus used in the process of the invention may be any of the stainless steels which are available. Such steels are the nickel-chromium steels for example

5 Firth-Vickers FMB containing 18% chromium, 8.5% nickel, 2.75% molybdenum and FDP containing 18% chromium, 8.5% nickel, 0.6% titanium (percentages by weight) and like steels.

10 The peroxides employed may be hydrogen peroxide, peracetic acid, performic acid, tert-butyl hydroperoxide, or mixtures containing such peroxides. The quantities of such peroxides necessary to reduce the corrosion to the desired level (generally not more than 0.01 inch penetration per annum) will vary, depending on the nature of the stainless steel and the composition of the acid mixture and on the temperature employed in the heat treatment, but will in general not exceed 5% and be preferably less than 2%, by weight based on the organic acid mixture.

20 The distillation is otherwise carried out in any suitable manner, for instance as regards distillation temperatures, residence times, and separation of particular fractions and may be operated according to the process of our co-pending British Application No. 17600/53, Serial No. 771,992.

25 The following Example is given to illustrate the process of the invention.

EXAMPLE.

30 Stainless steel corrosion strips (FDP quality) were placed in the kettle and at the feed point of a continuous still employed for the removal of low boilers from a wet acid mixture obtained by the oxidation of paraffin hydrocarbons, of the composition:

35	Water ..	30—31% by weight
	Formic acid	10% " "
	Acetic acid	55% " "
	C ₃ —C ₄ acids	3% " "
40	Neutrals (mostly low-boilers)	1—2% " "

The continuous distillation was divided into two periods 1, with no additives to the feed; 2, with hydrogen peroxide (35% w/v) added to the feed to the extent of 1% v/v. The corrosions measured are shown in the following table:—

Position of Strip	Corrosion Penetration (inches $\times 10^{-3}$ /year)	
	Period 1	Period 2
Feedpoint	160	nil
Kettle	260	nil

WHAT WE CLAIM IS:—

1. A process for the distillation, in apparatus constructed at least in part of stainless steel, of a mixture of lower aliphatic acids, including a minor proportion of formic acid, obtained by the oxidation with molecular oxygen of hydrocarbons or ketones, in which corrosion of the stainless steel is minimised by the addition of a peroxide to the mixture.

2. A process as claimed in Claim 1 wherein the mixture of aliphatic acids contains less than 25% by weight of formic acid.

3. A process as claimed in either of the preceding claims wherein the peroxide is hydrogen peroxide, peracetic acid, performic acid, or *t*-butyl hydroperoxide.

4. A process as claimed in any of the preceding claims wherein the peroxide is added to the feed to the still in a concentration of not more than 5% by weight.

5. A process as claimed in any of the preceding claims wherein the peroxide is added to the feed to the still in a concentration of not more than 2% by weight.

N. F. BAKER,
Agent for the Applicants.

PROVISIONAL SPECIFICATION.

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ing formic acid, acetic acid and other aliphatic acids; in particular formic acid is highly corrosive. As a result stainless steel is a usual material for the construction of apparatus to be used for such operations. Stainless steel, however, is corroded by formic acid, and investigations have been made to determine the conditions under which this corrosion will be a minimum. These investigations have shown (Lane, Golden and Acheman, Industrial & Engineering Chemistry, 1953, Volume 45, page 1067), that the corrosion of stainless steel by hot formic acid is a maximum in the presence of air and a minimum in the absence

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20 The distillation is otherwise carried out in any suitable manner, for instance as regards distillation temperatures, residence times, and separation of particular fractions and may be operated according to the process of our co-pending British Application No. 17600/53, Serial No. 771,992.

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The continuous distillation was divided into two periods 1, with no additives to the feed; 2, with hydrogen peroxide (35% w/v) added to the feed to the extent of 1% v/v. The corrosions measured are shown in the following table:—

Position of Strip	Corrosion Penetration (inches $\times 10^{-3}$ /year)		50
	Period 1	Period 2	
Feedpoint	160	nil	
Kettle	260	nil	

WHAT WE CLAIM IS:—

1. A process for the distillation, in apparatus constructed at least in part of stainless steel, of a mixture of lower aliphatic acids, including a minor proportion of formic acid, obtained by the oxidation with molecular oxygen of hydrocarbons or ketones, in which corrosion of the stainless steel is minimised by the addition of a peroxide to the mixture. 55

2. A process as claimed in Claim 1 wherein the mixture of aliphatic acids contains less than 25% by weight of formic acid. 65

3. A process as claimed in either of the preceding claims wherein the peroxide is hydrogen peroxide, peracetic acid, performic acid, or *t*-butyl hydroperoxide. 70

4. A process as claimed in any of the preceding claims wherein the peroxide is added to the feed to the still in a concentration of not more than 5% by weight. 75

5. A process as claimed in any of the preceding claims wherein the peroxide is added to the feed to the still in a concentration of not more than 2% by weight.

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of air, and these findings have been verified by the applicants.

It is an object of the present invention to provide a process involving the heat treatment of aliphatic acids obtained by the oxidation of hydrocarbons or ketones, containing formic, acetic and other acids, in apparatus constructed at least in part of stainless steel, in which the corrosion of stainless steel is reduced to a minimum.

Accordingly the present invention is for a process involving the heat treatment in apparatus constructed at least in part of stainless steel, of a mixture of aliphatic acids including a minor proportion of formic acid obtained by the oxidation with molecular oxygen of hydrocarbons or ketones in the presence of added peroxides.

The heat treatment involved is most usually a distillation operation. The process of the invention however is not restricted to distillations, but may equally be applied to other operations involving the heat treatment of mixtures of aliphatic acids.

The mixture of aqueous aliphatic acids containing a minor proportion of formic acid generally comprises an aqueous mixture of formic, acetic, propionic and butyric acids wherein the formic acid content is less than about 25% by weight of the mixture. Such acid mixtures are obtained for example by the processes described in co-pending British Applications Nos. 25789/52 (S.N. 743,989), 25792/52 (S.N. 743,990) and 25794/52 (S.N. 743,991) which relate to the production of aliphatic acids by the oxidation of lower paraffinic hydrocarbons. In such oxidations, ketones such as acetone and methyl ethyl ketone are intermediate products and accordingly ketones may serve as starting materials in the oxidation reaction to produce the mixture of aliphatic acids to be treated according to the invention. The oxidation product is usually submitted to a series of distillation steps to recover the acids, and the invention is useful with any of the acid-containing mixtures so obtained, as well as with the oxidation product itself. Even during the distillation of formic acid from higher acids, the invention may be used to reduce corrosion in at least the base of the still and the lower parts of the column.

The stainless steel employed in the construction of the apparatus used in the process

of the invention may be any of the stainless steels which are available. Such steels are the nickel-chromium steels for example Firth-Vickers FMB containing 18% chromium, 8.5% nickel, 2.75% molybdenum and FDP containing 18% chromium, 8.5% nickel, 0.6% titanium and like steels.

The peroxides employed may be hydrogen peroxide, peracetic acid, performic acid, tert-butyl hydroperoxide and the like, or mixtures containing such peroxides, or yielding such peroxides when contacted with the mixture of aliphatic acids. The quantities of such peroxides necessary to reduce the corrosion to the desired level will vary, depending on the nature of the stainless steel and the composition of the acid mixture and on the temperature employed in the heat treatment, but will in general not exceed 5% and be preferably less than 2%.

EXAMPLE.

Stainless steel corrosion strips (FDP quality) were placed in the kettle and at the feed point of a continuous still employed for topping a wet acid mixture obtained by the oxidation of paraffin hydrocarbons of the composition:—

Water	..	30—31%	
Formic acid	..	10%	
Acetic acid	..	55%	
C ₃ —C ₄ acids	..	3%	85
Neutrals	..	1—2%	

The continuous distillation was divided into two periods, 1, with no additives to the feed; 2, with hydrogen peroxide (35% w/v) added to the feed to the extent of 1% v/v.

The corrosions measured are shown in the following table:—

Position of Strip	Corrosion Penetration (inches $\times 10^{-2}$ /year)		95
	Period 1	Period 2	
Feedpoint	160	nil	
Kettle	260	nil	

N. F. BAKER,
Agent for the Applicants.