INSTRUCTIONS
(a) If Convention application insert "Convention"

341 378 83

(b) Delete one

(c) Insert FULL name(s) of applicant(s)

(d) Insert FULL address(es) of applicant(s)

(e) Delete one

(f) Insert TITLE of invention

(g) Insert "complete" OR "provisional" OR "petty patent"

(h) Insert number, country and filing date for the/OR EACH basic application

(i) Insert DATE of signing

(j) Signature of applicant(s)
(For body corporate see headnote*)

(k) Corporate seal if any

(Note: The following applies only to Convention applications)

Details of basic application(s)

<table>
<thead>
<tr>
<th>Application No.</th>
<th>Country</th>
<th>Filing Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>342,964</td>
<td>UNITED STATES OF AMERICA</td>
<td>26 January, 1982</td>
</tr>
</tbody>
</table>

Address for Service:

PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia 3000

Dated (i) 11 January, 1983

(j) PHILLIPS ORMONDE AND FITZPATRICK
Attorneys for:-
The Dow Chemical Company

Note: No legalization or other witness required

PEM:FC

PHILLIPS ORMONDE AND FITZPATRICK
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Melbourne, Australia

STUART TAYLOR
DECLARATION FOR A PATENT APPLICATION

In support of the (a) Convention application made by
(b) THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, U.S.A.

(hereinafter called "applicant(s)"
for a patent (e)

invention entitled (d) REMOVAL OF TRACE ALDEHYDES FROM UNSATURATED CARBOXYLIC ACIDS

I, we (c) Richard Gordon Waterman, General Patent Counsel,
THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, UNITED STATES OF AMERICA
do solemnly and sincerely, declare as follows:

1. I am/We are the applicant(s) —
   (or, in the case of an application by a body corporate)
1. I am/We are authorized to make this declaration on behalf of the applicant(s).
2. I am/We are the actual inventor(s) of the invention —
   (or, where the applicant(s) is/are not the actual inventor(s))
2. BONNIE KAYE METTETAL, 233 Success Street, Richwood;
   RICHARD PAUL KOLONKO JR., 106 Chestnut, Lake Jackson;
   both of County of Brazoria, State of Texas, United States of America

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

(a) The applicant Company is the assignee of the said invention from the said actual inventor(s).

(Note: Paragraphs 3 and 4 apply only to Convention applications)

3. The basic application(s) for patent or similar protection on which the application is based is/are identified by country, filing date, and basic applicant(s) as follows:
   U.S. Application Serial No. 342,964 which was filed on January 26, 1982 in the names of Bonnie Kaye Mettetal and Richard Paul Kolonko, Jr. in the UNITED STATES OF AMERICA

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Declared at (a) Midland, Michigan 48640,
Dated (b) January 3, 1983

THE DOW CHEMICAL COMPANY

By: Richard Gordon Waterman
   General Patent Counsel

No Legalization
1. A process for removing aldehydic impurities from an unsaturated acid by adding a compound to said acid which will react with said impurities, characterized by employing a 1,2-glycol as said added compound, reacting by heating and subsequently distilling the unsaturated acid to obtain an acid having a lower content of aldehydic impurities.
The following statement is a full description of this invention, including the best method of performing it known to applicant(s):
In the manufacture of carboxylic acids, frequently aldehydes are produced as by-product impurities. This is especially true in the process by which olefins are oxidized with molecular oxygen to produce unsaturated acids, where aldehydes are produced as an intermediate and these frequently are found in the end-product acid. Thus, acrolein is found as a minor impurity which is difficult to remove completely by distillation from acrylic acid. Also, such by-products are not removed completely by the extraction process normally used as part of the purification process.

Acrolein, and other aldehydic compounds, e.g., acetaldehyde, furfural, glyoxal and crotonaldehyde, are undesirable in the unsaturated acids when these are used for making polymers and plastics because they cause (1) a prolonged induction period in the polymerization reaction, (2) color in the resulting products made from these polymers, (3) cross-linking, and (4) chain termination which results in lower molecular weight polymers.
Various methods are suggested in the art for removing these aldehydic impurities from the acids. For example, U.S. Patent 3,725,208 (Maezawa et al., April 3, 1973) discloses a method whereby sulfuric acid, hydrazine, phenylhydrazine, aniline, monoethanolamine, ethylene diamine or glycine are added to the acid prior to its distillation. Another patent, U.S. Patent 3,893,895 (Dehnert et al., July 8, 1975) claims reacting the aldehydic compounds with aliphatic or aromatic amines, such as hydroxylamine, a monoalkylamine, or naphthylamine to chemically bind the aldehydic compounds and then recovering said carboxylic acid by distillation. In such processes, some of the amine reacts with the acid as well as with the aldehydes present, with consequent loss in yield of the acid.

It has now been discovered that some of the aldehydic impurities in unsaturated acids selectively react with 1,2-glycols added to the acid and, upon subsequent distillation, can be removed (since the product remains in the bottoms) with no loss of unsaturated acid product.

The present invention is a process for removing aldehydic impurities from an unsaturated acid by adding a compound to said acid which will react with said impurities, characterized by employing a 1,2-glycol as said added compound, reacting by heating and subsequently distilling the unsaturated acid to obtain an acid having a lower content of aldehydic impurities.
The addition of a 1,2-glycol to an unsaturated acid prior to its distillation will, upon heating the mixture during distillation, react with the aldehydic impurities and allow them to remain in the bottoms of the distillation column. The acid distillate contains much less of the aldehydic impurities with no loss in yield of the desired acid.

Unsaturated acids, because of their tendency to polymerize with heat, are generally distilled under vacuum at low temperatures. The addition of the glycol does not at all affect the conditions under which the purification by distillation takes place. Pressures of 20 to 30 mm Hg are employed and vapor temperatures of from about 30°C to about 40°C are used in the purification, depending on the particular acid used. Pot temperatures no more than about 30°C-40°C greater than the vapor temperature are employed in the distillation. The glycol is added in at least an amount equivalent to the aldehydic content, but no more than about 1.0 percent based on the weight of the acid.

The process of the invention is suited for the purification of 1,2-unsaturated carboxylic acids (e.g., alkenoic acids), preferably those 1,2-unsaturated carboxylic acids having 3 to 6 carbon atoms in the chain, especially those having 3 to 4 carbon atoms such as acrylic acid and methacrylic acid. Other unsaturated acids which can be purified include ethacrylic acid and alpha hexenoic acid.
The acids can be preliminarily purified by the customary measures such as extraction and distillation before use of the process of the invention, especially to reduce the content of aldehydic compounds, i.e., aldehydes below about 5 percent, based on the weight of the acid, preferably to below about 2 percent. The process of the invention is especially suited to the purification of all unsaturated carboxylic acids produced by vapor phase oxidation of an alkene or alkenal and which are largely freed of by-products by known processes. This type of recovered unsaturated carboxylic acid generally contains less than 2 percent, based on the weight of the acid, for the most part less than 1 percent of aldehydic compounds. The aldehydic compounds, for example, in the case of acrylic acid are acrolein, formaldehyde, acetaldehyde, glyoxal and furfural. Other carbonyl compounds which can be removed include, for example, methacrolein, crotonaldehyde, and hexen-2-al.

The reaction of the glycol with the aldehydic impurities is believed to form cyclic acetals of the formula

\[
\begin{align*}
\text{R}_1 & \quad \text{C} \quad \text{R}_2 \\
\text{O} & \quad \text{C} \quad \text{R}_3
\end{align*}
\]

wherein \( \text{R}_1, \text{R}_2 \) and \( \text{R}_3 \) are lower alkyl groups, having from 1 to 3 carbon atoms; \( \text{R}_1 \) and \( \text{R}_3 \) can be hydrogen; and \( \text{R}_2 \) can be alkenyl.
These acetals are heavier compounds having higher boiling points than the acid and thus remain in the bottoms of the distillation process.

The following example illustrates the process of the present invention.

Example 1

Into a one-liter glass distillation pot fitted with a distillation column, having approximately 10 plates and cooled with ice water, was placed 1060.4 g of crude acrylic acid from a propylene oxidation process and to this was added 10.76 g (1.01 percent by weight) of ethylene glycol. The aldehydic content was 0.98 percent by weight in the undistilled acid. After distillation in the presence of the glycol under a pressure of 20 mm Hg and at a vapor temperature of 33°C, the aldehydic content of the distillate was 0.038 percent by weight, a decrease of 96 percent in aldehydic content.
The claims defining the invention are as follows:

1. A process for removing aldehydic impurities from an unsaturated acid by adding a compound to said acid which will react with said impurities, characterized by employing a 1,2-glycol as said added compound, reacting by heating and subsequently distilling the unsaturated acid to obtain an acid having a lower content of aldehydic impurities.

2. The process of Claim 1 and further characterized in that the unsaturated acid contains from 3 to 6 carbon atoms.

3. The process of Claim 2 and further characterized in that the unsaturated acid contains from 3 to 4 carbon atoms.

4. The process of Claim 3 and further characterized in that the unsaturated acid is acrylic acid.

5. The process of Claim 1 and further characterized in that the 1,2-glycol is ethylene glycol.
5. The process of any one of claims 1 to 4, further characterized in that the 1,2-glycol is ethylene glycol.
6. The process of any one of claims 1 to 5, further characterized in that the distillation is conducted under reduced pressure.
7. The process of claim 1 substantially as hereinbefore described with reference to the example.

DATED: 20th August, 1987
PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:
THE DOW CHEMICAL COMPANY

[Handwritten signature]