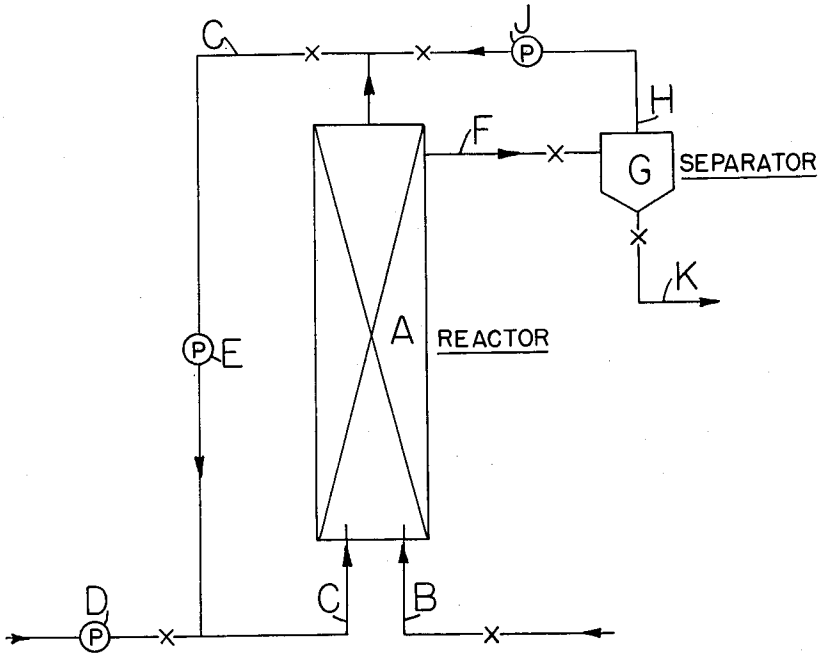
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PROCESS FOR PRODUCING ACRYLIC ACID

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PROCESS FOR PRODUCING ACRYLIC ACID

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This invention relates to the production of acrylic acid by the carbonylation of acetylene in the presence of water, and more particularly, to an improved method of producing acrylic acid in a novel aqueous reaction medium containing an activated carbonylation catalyst.

It has already been proposed to produce acrylic acid by bringing acetylene and carbon monoxide into contact with water in the presence of catalytic quantities of compounds of metals of the Iron Group, i.e. iron, nickel or cobalt, the reaction being carried out under super-atmospheric pressures and at elevated temperatures. The same type of catalytic reaction has also been employed in the production of acrylic acid esters by substituting alcohols in place of water. The improved production of such acrylic acid esters forms the subject matter of our copending application, Serial No. 468,580, filed November 12, 1954 and issued as U.S. Patent 2,883,418. The present application is a continuation-in-part of our prior copending application, Serial No. 410,179, filed February 15, 1954, abandoned after the filing of this application.

The catalytic methods of producing acrylic acid and acrylic acid esters are generally conceded to be superior to the vairous known stoichiometric methods in which nickel carbonyl in substantial amounts is required as an essential ingredient of the reaction mixture. Since nickel carbonyl is an expensive and poisonous compound, much time and effort has been devoted in research to find a commercially useful catalytic method whereby the use of nickel carbonyl can be avoided. Various modifications of the catalytic method have therefore been suggested, and while fairly satisfactory results have been obtained in the synthesis of acrylic acid esters, the results when producing acrylic acid itself have been especially disappointing and unsatisfactory on an industrial scale. It has been our observation that the acetylene employed as a starting material tends to be transformed into acetaldehyde during the synthesis of acrylic acid. The activity of the known catalysts under known reaction conditions thereby decreases relatively quickly so as to substantially reduce the rate of conversion with correspondingly low yields.

The prior art, including that appearing in our copending parent application, which is pertinent to the manufacture of acrylic acid may be set forth as follows:

In the manufacture of acrylic compounds such as acrylic acid or acrylic acid esters by the so-called stoichiometric method (German Patents 855,110, 872,042, 872,341 and 872,939), stoichiometric amounts of a metal carbonyl are reacted with acetylene an a compound with a reactive hydrogen atom such as water or an alcohol in the presence of an acid. This process can be illustrated by the following equation:

$$C_2H_2+\tfrac{1}{4}Ni(CO)_4+H_2O+\tfrac{1}{2}HCl = CH_2=CH-COOH+\tfrac{1}{4}NiCl_2+\tfrac{1}{4}H_2$$

It is a disadvantage of this process that the entire carbon monoxide required for the carbonylation of the acetylene must be furnished by the expensive and poisonous metal carbonyls.

In the production of acrylic acid and its esters by the so-called catalytic method (German Patents 854,948, 881,650 and 805,641, copending application Serial No. 288,534, now Patent 2,738,364, and J. W. Reppe, Acetylene Chemistry, C. A. Meyer & Co., Inc., New York (1949), page 161), acetylene, free carbon monoxide and a compound with a reactive hydrogen atom are reacted in the presence of catalytic amounts of carbonyl-forming metals or the oxides or salts of such metals. For the formation of acrylic acid this process can be illustrated by the equation

$$C_2H_2+CO+H_2O \xrightarrow{\text{catalyst}} CH_2=CH-COOH$$

While nickel carbonyl is the most suitable catalyst in such a process it has the disadvantage of favoring the formation of by-products such as acetaldehyde and vinylbromide.

Various additives such as metals, metal compounds or complex-forming organic compounds of phosphorus, arsenic, antimony and nitrogen have been suggested in order to increase the activity and the life of the catalyst employed in the catalytic synthesis of acrylic compounds from acetylene, carbon monoxide and compounds containing a reactive hydrogen atom.

These processes yield fairly satisfactory results when employed for the synthesis of acrylic acid esters. However, in the production of free acrylic acid, such processes work only with low yields and poor throughputs. Furthermore, the carbonyl-forming metal catalysts such as nickel halides have been employed according to the prior art in relatively high amounts and the catalyst forms thereby with the liquid reaction medium a non-homogeneous system.

U.S. Patent 2,613,222 shows the preparation of acrylic acid and its anhydrides by a process in which the catalytic reaction between water, acetylene and carbonyl monoxide must be first initiated by a stoichiometric interaction between water, acetylene, nickel carbonyl and an acid. The stoichiometric reaction which precedes the catalytic reaction must furthermore be maintained while there is imposed upon it the catalytic reaction. In such a process at least 35%, but preferably 40% to 50% of the total carbon monoxide is carbon monoxide supplied by nickel carbonyl.

It is a disadvantage of this process that a great deal of the reaction must be performed by the stoichiometric method which entails a high demand of pre-formed nickel carbonyl, therefore requiring particular safety measures.

One object of the invention is to avoid the formation of by-products, especially acetaldehyde, in the production of acrylic acid by employing a particular activated catalyst.

Another object of the invention is to provide an improved production of acrylic acid in which the catalyst has a long life and its activity is increased and maintained.

Yet another object of the invention is to produce acrylic acid with a specific catalyst and under reaction conditions, including the use of a novel aqueous reaction medium, whereby high throughputs can be obtained.

Together with the foregoing objects, a principal object of the invention is to provide a process for the production

of acrylic acid on a large scale. These and other objects and advantages of the invention will become more apparent upon a consideration of the following detailed specification.

We have found in accordance with the present invention that in carrying out the carbonylation of acetylene in the presence of water it is very advantageous to use an excess by volume of an organic solvent with reference to the volume of water employed, said organic solvent being inert to acetylene under the reaction conditions and miscible with water. We have further found that the amount of the carbonylation catalyst, i.e. of a compound derived from a metal of the Iron Group, should be so chosen that this catalyst is homogeneously dissolved in the liquid reaction medium constituted by the mixture of water and inert organic solvent. It has also been established by us that the catalysts should be activated by including in the reaction medium a small amount of a soluble copper compound.

As organic solvents we prefer oxygen-containing water-miscible liquids which are inert under the reaction conditions, i.e. which are not irreversibly changed by the presence of water and which are not able to react with acetylene or carbon monoxide. The solvents, therefore, should not contain free hydroxy, mercapto or carboxy groups, olefinic or acetylenic linkages, or primary or secondary amino groups. Their boiling point should preferably be below that of acrylic acid, i.e. below about 142° C. Preferred solvents for our process are cyclic ethers, such as tetrahydrofurane, -pyrane and 1,4-dioxane, and also fully saturated aliphatic ketones, such as acetone, methyl ethyl and diethyl ketone. Another group of useful solvents consists of cyclic esters and amides, such as butyrolactone or N-lower alkyl-lactams, in particular N-alkyl-pyrrolidones, such as the methyl and ethyl compounds. Tetrahydrofurane, whenever available, is a very satisfactory solvent, since it has a relatively low boiling point and a high dissolving power for acetylene, and is otherwise absolutely inert. It may be easily and cheaply recovered and used again.

While in our process it is possible to work with a slight excess of the solvent, e.g. 60 parts by volume for 40 parts by volume of water, we prefer to employ much higher excesses of the organic solvent in the working liquid. We suggest to have from 75 to 95 percent by volume of the solvent and from 25 to 5 percent of water. With some solvents, especially tetrahydrofurane, it is quite satisfactory to work with from 10 to 15 percent by volume of water. It is also possible to work with mixtures of two or more organic solvents.

The catalysts used in performing our invention are compounds of metals of the iron group. While both iron and cobalt show carbonylation activity which makes them potential technical catalysts, we prefer to work with nickel compounds. Since the catalysts should in any case contain halogen either in a free or in a chemically combined form, the simplest way is to use the halides, especially nickel chloride and bromide and iodides. The iodides are very active, but some care must be exercised to avoid corrosion. We may also use metal carbonyls prepared per se, provided there is present halogen, e.g. free bromine, hydrogen bromide, halides of other metals and the like. Thus, mixtures of nickel, cobalt or iron carbonyls in combination with other metal halides are workable catalysts. At the same time, it is a special advantage of the invention that such metal carbonyls can be avoided, their inclusion herein merely illustrating the use of soluble nickel compounds. We may also build up our catalyst from several metals of the Iron Group.

As activators we use copper compounds which are soluble in the reaction medium. Since the reaction has to be carried out in the presence of halogen, it is preferred to use the copper as a halide, e.g. chloride, bromide or iodide. Copper sulfate, acetate, propionate and other water-soluble salts may be used together with halide ions. Sometimes it has been found useful to add a small amount (less than 1 percent by weight) of powdered copper. However, the process works generally quite satisfactorily without it. Furthermore, a small amount of halogen hydride, e.g. 0.1 to 1 percent by weight of hydrogen bromide, is useful.

The amount of the catalyst required is relatively small and depends to some extent on the kind of metal, which compound thereof is used, and on the composition of the liquid reaction medium. Generally speaking, the concentration is a catalytic quantity, i.e. not more than 2 percent and preferably not more than 0.5 percent by weight of the compound of the metal of the Iron Group, calculated on the liquid reaction medium. Satisfactory results have been obtained in the range of about 0.05 to 2 percent. The amount of the copper compound used as an activator is in general somewhat lower than that of the catalyst, i.e. usually not more than 0.1 percent by weight of the copper compound calculated on the liquid reaction medium. Satisfactory results have been obtained from about 0.02 percent by weight of the activator up to as much as an equal amount with reference to a nickel halide employed in the reaction medium.

The reaction conditions used in the carbonylation are within the conventional range. We prefer to use acetylene and carbon monoxide in substantially equimolecular ratios, but the C_2H_2:CO ratio may vary within wide limits, e.g. between 0.5:1 to 1:0.5. When working with a circulating gas, a 1:1 ratio is of advantage to avoid an accumulation of the excess component in the circulating gas.

The working temperature is in the range of 150° C. to 250° C., in particular between 170° C. and 220° C. The carbonylation requires the use of increased pressure. While in principle we may work at pressures exceeding 5 atmospheres, we found it more economic to ensure a high conversion rate by applying at least 20 atmospheres, e.g. up to 60 atmospheres, and an individual partial pressure for acetylene and carbon monoxide of at least 10 atmospheres. Pressure above 60 atmospheres, e.g. 70 to 90 atmospheres, may also be used. However, the precautions necessary when working with acetylene at very high pressures are generally so expensive that the gain in higher conversion tends to be cancelled.

The reaction may be carried out batchwise or continuously. In a continuous process we may either work according to the trickling method by leading the working liquid downwards through a reactor charged with filler bodies while leading the gas mixture in the same or opposite direction. We may as well introduce liquid and gases at the bottom of a reactor and withdraw the mixture at the top thereof. The recovery of acrylic acid from the reaction liquid is carried out either by extraction or by fractional distillation. In this stage as well as during the carbonylation stage proper we may add the conventional polymerization inhibitors.

The following examples will further illustrate how this invention may be carried out in practice.

Example 1

A stirring autoclave made from stainless steel is charged with 2,500 cubic centimeters of tetrahydrofurane, 270 cubic centimeters of water, 6 grams of anhydrous nickel bromide, 1.5 grams of copper chloride and 0.3 gram of hydroquinone. After having replaced the air by nitrogen, a mixture of equal parts by volume of acetylene and CO under 25 atmospheres is pressed in and the whole heated to 180° C. in the course of about 90 minutes, thereby increasing the pressure to 46 atmospheres. By drawing a sample, homogeneousness of the working liquid is confirmed. As the reaction starts, it is accompanied by an increase in temperature and a decrease in the pressure. The temperature is maintained at from 184° to 188° C. and the pressure at from 44 to 50 atmospheres by replenishing the gas mixture. After

2 hours the reaction is finished. The reaction mixture is then released from pressure (the release gas contains a little CO_2) and distilled. 544 grams of acrylic acid are thus obtained and 56 grams of higher boiling products.

When working under otherwise identical conditions with 5 grams of nickel chloride and 2 grams of copper bromide, the reaction takes a little longer. The yield amounts to 538 grams of acrylic acid.

Example 2

A homogeneous mixture of 2,365 cubic centimeters of tetrahydrofurane, 265 cubic centimeters of water, 4.55 grams of nickel carbonyl, 1.82 grams of copper bromide and 0.9 gram of hydrogen bromide are treated with acetylene and CO (1:1.1) at from 186° to 196° C. under 40 to 50 atmospheres. In the course of one hour, 656 grams of acrylic acid (86.8 percent yield) are formed. The high boiling residue contains the total of the nickel in the form of acrylate. A small amount of acetaldehyde is to be found in the first distillation fraction.

When changing the ratio of C_2H_2:CO to 1:1 or 1.1:1, the results are substantially identical. When working in the absence of hydrogen bromide, the amount of high boiling residue is somewhat larger.

Example 3

In a shaking autoclave made from stainless steel a mixture of 90 cubic centimeters of tetrahydrofurane, 10 cubic centimeters of water, 0.2 gram of nickel chloride and 0.2 gram of copper chloride is treated in the manner described in Example 2 with a mixture of acetylene and CO at 195° C. under 45 to 50 atmospheres for 2 hours. 15 grams of acrylic acid are formed. When working with 85 cubic centimeters of tetrahydrofurane and 15 cubic centimeters of water and continuing the reaction for another hour, 19 grams of acrylic acid are formed.

Example 4

A stirring autoclave is charged with the following mixture: 2,360 cubic centimeters of tetrahydrofurane, 240 cubic centimeters of water, 3.6 grams of iron carbonyl, 1.8 grams of copper bromide, 2 grams of bromine and 0.3 gram of hydroquinone. In the manner described in Example 1 the mixture is treated at 200° to 208° C. with acetylene and CO (1:1) for 2 hours. There are obtained 631 grams of acrylic acid, 150 grams of higher boiling products and a very small quantity of acetaldehyde.

When working with iron bromide under otherwise identical conditions, the addition of bromine may be dispensed with.

Example 5

In a stirring autoclave a solution consisting of 2,360 cubic centimeters of tetrahydrofurane, 240 cubic centimeters of water, 2.27 grams of nickel carbonyl, 0.15 gram of iron carbonyl, 1.65 grams of copper bromide and 1 gram of bromine is treated for 1 hour at 184° to 193° C. with acetylene and CO (1:1) under 40 to 50 atmospheres. Acrylic acid (598 grams) is obtained in an 88.5 percent yield together with 77 grams of higher boiling products.

Example 6

Under the conditions of Example 4, a mixture of 60 cubic centimeters of tetrahydrofurane, 7 cubic centimeters of water, 0.1 gram of cobalt bromide and 0.1 gram of copper bromide is treated for 2 hours at 200° C. under 50 atmospheres. 7.74 grams of acrylic acid and 2.6 grams of higher boiling products are formed.

To obtain the same result with cobalt chloride instead of the bromide, the reaction time has to be increased to 3 hours.

Example 7

A homogeneous solution of 0.2 gram of nickel chloride and 0.2 gram of copper chloride in a mixture of 100 cubic centimeters of acetone and 14 cubic centimeters of water is treated in a shaking autoclave at 190° C. for 1 hour with a mixture of acetylene and CO (1:1) while maintaining a pressure of 50 atmospheres. By distillation of the reaction mixture there are obtained 20.25 grams of acrylic acid and 2.1 grams of higher boiling products.

Practically the same results are obtained when employing the bromides instead of the chlorides.

Example 8

A homogeneous solution of 0.1 gram of nickel bromide and 0.5 gram of copper chloride in 80 cubic centimeters of an aqueous 88 percent dioxane are heated to 195° to 197° C. while pressing in a mixture of acetylene and CO under a pressure of 40 to 51 atmospheres. After 2 hours the reaction is finished. The working solution then contains 20.9 percent by weight of acrylic acid which is isolated by distillation.

Example 9

This example demonstrates a continuous process.

Referring to the drawing, the reactor A, preferably a pressure-tight tube made from stainless steel and provided with heating and cooling devices (not shown), is charged with the working liquid (solvent, water and catalyst) through tube B. Through tube C a mixture of acetylene and carbon monoxide is pressed into the reaction zone A by means of pump D. The reactor is then brought to reaction temperature while maintaining the gas pressure. After the reaction has started which will be evident from consumption of gas and the evolution of heat, the feeding of gas is continued and circulation maintained through line C via pump E.

When the acrylic acid concentration in the liquid has reached a certain level, e.g. between 10 and 20 percent by weight, fresh working liquid is introduced through B and a corresponding amount of acrylic acid solution withdrawn through F. It is brought into a separator G where the pressure is released. The gases set free are brought back through line H and pump J into the main circulation line C. The acrylic acid solution is withdrawn through line K and introduced into a distillation apparatus (not shown).

A stainless steel tube of 10 centimeters internal diameter and 6 meters length (reactor A) to which lines for feeding and withdrawing gas and liquid are attached is filled with 30 liters of a working liquid consisting of tetrahydrofurane, containing 12 to 15 percent of water, 0.16 percent of nickel bromide, 0.05 percent of copper bromide, 0.1 percent of hydrogen bromide and 0.01 percent of hydroquinone. The reactor is slowly heated and acetylene-carbon monoxide mixture (1:1) under 46 atmospheres is pressed in.

The carbonylation starts slowly at about 170° to 180° C. and the temperature is allowed to increase to 200° to 205° C. while always maintaining 46 atmospheres. After about one hour the acrylic acid concentration has reached 20 percent. Now 28 liters per hour of fresh working liquid are introduced and about 30 to 31 liters per hour of acrylic acid solution withdrawn. Fresh gas mixture is introduced at the rate of 5 cubic meters (N.T.P.) per hour.

The acrylic acid solution is withdrawn, and the acid isolated by distillation. The tetrahydrofurane obtained as the first fraction is used again, after adding the other ingredients of the working solution.

From the foregoing description and examples, it can readily be determined that our catalytic process for producing acrylic acid shows an extraordinary improvement over prior processes. Throughput and yield of acrylic acid is substantially increased. A special advantage of

the invention resides in the use of inexpensive and readily obtainable catalysts and activators, the nickel and copper halides being especially preferred to obtain optimum results. Of course, other nickel and copper compounds which are soluble in the reaction medium can also be employed in catalytic amounts.

It will also be noted that our improvement in the production of acrylic acid essentially requires a substantial excess of an inert water miscible organic solvent with relation to water in the aqueous reaction medium and furthermore requires a catalyst in which nickel, halogen and copper must be present and dissolved to produce a homogeneous reaction mixture with the organic solvent and water. Under these conditions and the specified temperatures and at high pressures it has been possible to provide a process which can be easily carried out on a large scale.

We claim:

1. A process for the production of acrylic acid which consists essentially of contacting a gaseous mixture of acetylene and carbon monoxide under a pressure exceeding 5 atmospheres and at temperatures between 150° and 250° C. with an aqueous reaction mixture of water containing at most 40% by volume of water and at least 60% by volume of an organic, water-miscible inert solvent with respect to the total volume of said water and said solvent, said aqueous reaction mixture having homogeneously dissolved therein ions of a metal of the Iron group, halide ions from the group consisting of chloride, bromide and iodide, and copper ions.

2. A process for the production of acrylic acid which consists essentially of contacting a gaseous mixture of acetylene and carbon monoxide under a pressure exceeding 5 atmospheres and at temperatures between 150° and 250° C. with an aqueous reaction mixture of water containing at most 40% by volume of water and at least 60% by volume of an organic, water-miscible inert solvent with respect to the total volume of said water and said solvent, said aqueous reaction mixture having homogeneously dissolved therein nickel ions, halide ions from the group consisting of chloride, bromide and iodide, and copper ions.

3. A process for the production of acrylic acid which consists essentially of contacting a gaseous mixture of acetylene and carbon monoxide under a pressure exceeding 5 atmospheres and at temperatures between 150° and 250° C. with an aqueous reaction mixture of water containing at most 40% by volume of water and at least 60% by volume of an organic, water-miscible inert solvent, with respect to the total volume of said water and said solvent, said aqueous reaction mixture having homogeneously dissolved therein a carbonylation catalyst consisting essentially of a nickel halide from the group consisting of nickel chloride, nickel bromide and nickel iodide and a copper halide from the group consisting of copper chloride, copper bromide and copper iodide.

4. A process as set forth in claim 3, wherein one of the halides is a bromide and the other is a chloride.

5. A process for the production of acrylic acid which consists essentially of contacting a gaseous mixture of acetylene and carbon monoxide under a pressure of at least 20 atmospheres and at a temperature between 170° and 220° C. with an aqueous reaction mixture containing between 5 and 25 percent by volume of water and between 95 and 75 percent by volume of an organic, water-miscible inert solvent, said aqueous reaction mixture having homogeneously dissolved therein not more than 2 percent by weight of nickel in the form of a nickel halide from the group consisting of nickel chloride, nickel bromide and nickel iodide and at most an equal amount of the copper halide from the group consisting of copper chloride, copper bromide and copper iodide.

6. A process as set forth in claim 5, wherein one of the halides is a bromide and the other is a chloride.

7. A process as set forth in claim 5, wherein bromides are used as the halides.

8. A process as set forth in claim 5, wherein chlorides are used as the halides.

9. A process for the production of acrylic acid which consists essentially of contacting a gaseous mixture of acetylene and carbon monoxide under a pressure of at least 20 atmospheres and at a temperature between 170° and 220° C. with an aqueous reaction mixture containing between 5 and 25 percent by volume of water and between 95 and 75 percent by volume of tetrahydrofurane, said aqueous reaction mixture having homogeneously dissolved therein ions of a metal of the Iron group, halide ions from the group consisting of chloride, bromide and iodide, and copper ions.

10. A process for the production of acrylic acid which consists essentially of contacting a gaseous mixture of acetylene and carbon monoxide under a pressure of at least 20 atmospheres and at a temperature between 170° and 220° C. with an aqueous reaction mixture containing between 5 and 25 percent by volume of water and between 95 and 75 percent by volume of tetrahydrofurane, said aqueous reaction mixture having homogeneously dissolved therein cobalt ions, halide ions from the group consisting of chloride, bromide and iodide, and copper ions.

11. A process for the production of acrylic acid which consists essentially of contacting a gaseous mixture of acetylene and carbon monoxide under a pressure of at least 20 atmospheres and at a temperature between 170° and 220° C. with an aqueous reaction mixture containing between 5 and 25 percent by volume of water and between 95 and 75 percent by volume of tetrahydrofurane, said aqueous reaction mixture having homogeneously dissolved therein iron ions, halide ions from the group consisting of chloride, bromide and iodide, and copper ions.

12. A process for the production of acrylic acid which consists essentially of contacting a gaseous mixture of acetylene and carbon monoxide under a pressure of at least 20 atmospheres and at a temperature between 170° and 220° C. with an aqueous reaction mixture containing between 5 and 25 percent by volume of water and between 95 and 75 percent by volume of tetrahydrofurane, said aqueous reaction mixture having homogeneously dissolved therein nickel ions, halide ions from the group consisting of chloride, bromide and iodide, and copper ions.

13. A process for the production of acrylic acid which consists essentially of contacting a gaseous mixture of acetylene and carbon monoxide under a pressure of at least 20 atmospheres and at a temperature between 170° and 220° C. with an aqueous reaction mixture containing between 5 and 25 percent by volume of water and between 95 and 75 percent by volume of tetrahydrofurane, said aqueous reaction mixture having homogeneously dissolved therein a carbonylation catalyst consisting essentially of a nickel halide from the group consisting of nickel chloride, nickel bromide and nickel iodide and a copper halide from the group consisting of copper chloride, copper bromide and copper iodide.

14. A process as set forth in claim 13, wherein one of the halides is a bromide and the other is a chloride.

15. A process as set forth in claim 13, wherein bromides are used as the halides.

16. A process as set forth in claim 13, wherein chlorides are used as the halides.

17. A process for the production of acrylic acid which consists essentially of leading continuously through a vertically orientated reaction zone under a pressure of at least 20 atmospheres and at temperatures between 170° and 220° C. a gaseous mixture of acetylene and carbon monoxide and a liquid constituting an aqueous reaction mixture of from 10 to 20 percent by volume of water and from 90 to 80 percent by volume of tetrahydrofurane, said aqueous reaction mixture having dissolved therein not more than 0.5 percent by weight of a nickel halide from the group consisting of nickel chloride, nickel bro-

mide and nickel iodide and not more than 0.1 percent by weight of a copper halide from the group consisting of copper chloride, copper bromide and copper iodide, releasing the pressure from the liquid withdrawn from said reaction zone, and separating acrylic acid from the liquid.

18. A process as claimed in claim 1 in which the halide ions are introduced at least in part by adding to such reaction mixture a free halogen from the group consisting of chlorine, bromine and iodine.

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