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"Manufacture of Arsenic Acid"

The present invention relates to a process for the manufacture of arsenic acid and, more particularly, to a process involving a new catalytic method.

5 Arsenic acid is generally understood as meaning the compound H_3AsO_4 , sometimes expressed as $H_3AsO_4 \cdot \frac{1}{2}H_2O$, and also known as ortho-arsenic acid. meta-Arsenic acid $HAsO_3$ and pyro-arsenic acid $H_4As_2O_7$ (also referred to as arsenic pentoxide hydrate $As_2O_5 \cdot 2H_2O$) are other forms
10 of arsenic acid, but both dissolve in water to form ortho-arsenic acid. The term "arsenic acid" as used herein refers primarily to ortho-arsenic acid but also includes the other arsenic acids where appropriate.

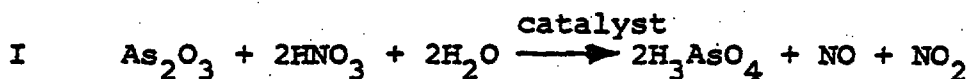
Arsenic acid has long been used as a pest
15 control agent in a variety of forms and applications including, for example, use in insecticides, herbicides and rodenticides, and use as a component of certain timber preservation products. It is also used in the manufacture of arsenates, in glass manufacture, as
20 a defoliant in certain circumstances, as a desiccant for cotton, and as a soil sterilant.

Many methods have been proposed for the industrial manufacture of arsenic acid and the large majority of those methods involve the oxidation of arsenic
25 trioxide As_2O_3 (also known as crude arsenic, white arsenic, arsenious acid, arsenious oxide, arsenous oxide, arsenous anhydride, and simply as "arsenic"). Oxidising agents that have been proposed for this purpose

include, for example chlorine (see US 1 415 323 - Ellis et al; US 1 447 937 - Ellis et al; and US 1 515 079 - Stewart), sodium or potassium chlorate (see US 1 677 257 - Ullmann et al; and US 1 699 823 - Ullmann et al), air or
5 oxygen (see GB 445 468 and US 1 992 053 - Boller, Grasselli Chemical Co.; JP 94024 (1931) - Chem. Abs. 27, 1456; and Khimiko Farmatsevticheskaya Promshlennost, 1933, 193 - 194 - Chem. Abs. 28, 428), and hydrogen peroxide (see SU 510 430 (1976) - Chem. Abs. 85, 35175t).
10 Oxidation by means of electrolysis has also been proposed (see SU 58371 (1940) - Chem. Abs. 38, 5736, and JP 9178 (1960) - Chem. Abs. 55, 20732).

The method that has become generally commercially used, however, involves oxidation with nitric acid.
15 Various catalysts or co-oxidants have been proposed for use in the nitric acid method including, for example, oxygen (see GB 255 522 and US 1 650 860 - Askenasy et al), hydrochloric acid (see US 1 493 798 - Behse; and SU 45279 (1935) - Chem. Abs. 32, 3100), air and water
20 (see US 1 615 193 - Piver), and air (see Chem. Abs. 55, 11776). The catalyst most commonly used in modern-day plants for the manufacture of arsenic acid by the nitric acid method is iodine in the form of, for example, sodium or potassium iodide (see US 1 974 747 - Latimer) or
25 potassium iodate (see Chem. Abs. 36, 3091).

The basic reaction occurring in the manufacture of arsenic acid by the known nitric acid method may be represented in simple form as follows:



The process is generally carried out by feeding arsenic trioxide, nitric acid and catalyst (for example, potassium iodide) continuously into a heated reactor at atmospheric
5 pressure, discharging the gaseous nitrogen oxides formed, and running off the arsenic acid formed.

A number of problems are encountered in carrying out that process on a large scale. One of those problems is the excessive foaming that tends to occur as a result
10 of the large volume of gaseous nitrogen oxides formed and, if foaming becomes excessive, there is a risk of a boil-over or blow-out occurring. Such a risk occurs particularly when there is a build-up in the reactor of large amounts of one or both unreacted starting
15 materials, which may occur if there is a feed blockage or other irregular feeding of one of the reactants or if the temperature of the reaction mixture should fall too low for some other reason.

Apart from the problems caused by excessive foaming,
20 the reaction is in any case difficult to control: considerable heat is evolved during the early stages of the process, whereas heat has to be supplied during the later stages. The reactor has to be heated up in advance of the reactants being added - often it is allowed
25 to heat up overnight - because there is a risk of sludging, and consequent later foaming and boil-over, occurring if

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there is an initial build-up of unreacted starting materials as a result of too low an initial temperature. On the other hand, the process cannot- because of its exothermic nature - readily be terminated prematurely if, 5 for example, it appears to be getting out of control. Furthermore, there is no simple indication of when the reaction has finished.

Various measures have been proposed for adding and mixing the reactants in a controlled manner in order 10 to overcome such difficulties (see, for example, US 1 603 308 - Ambruster; and US 2 165 944 - Scott) but the difficulties still occur even in modern plants, and they have to some extent been aggravated by the present need to use low-grade arsenic trioxide as a starting material.

15 Another serious disadvantage of the conventional nitric acid method is the need to use large amounts of nitric acid: it has to be supplied in a stoichiometric amount with respect to arsenic trioxide in accordance with equation I above; that is to say that 2 moles of 20 nitric acid are required per mole of arsenic trioxide. That means that, for example, the manufacture of an 8 tonne batch of 80% arsenic acid requires about 5 tonnes of commercial nitric acid, which is reduced to nitrogen oxides during the course of the process. Those nitrogen oxides 25 have to be reclaimed by reoxidation to nitric acid both for economic reasons and for health and safety reasons.

All plants manufacturing arsenic acid by the nitric acid method therefore include apparatus for recovering

the nitric acid. That may, for example, be a series of reaction towers connected directly to the main reactor and through which the gaseous nitrogen oxides issuing from the main reactor are passed for reaction with water and oxygen, and a final tower in which the gases are scrubbed with caustic soda to remove any residual nitrogen oxides. (Details of examples of nitric-acid-recovery apparatus are given in US 2 165 957 - Carter and JP 79.016943 - Ohya et al..) Because of the very large volumes of nitrogen oxides evolved during the course of the process, the nitric-acid-recovery apparatus constitutes a substantial proportion of the entire arsenic-acid-manufacturing plant and contributes appreciably to the overall cost of the resulting arsenic acid.

Moreover, even though the recovered nitric acid is recycled, there tends to be an overall loss of up to 10% of nitric acid. Thus, for example, a loss of about 500 kg of nitric acid would be expected in the manufacture of an 8 tonne batch of arsenic acid. That loss adds further to the cost of the final product, both because of the need to replace the lost nitric acid and also because of the need to scrub the gases with caustic soda to neutralise the nitrogen oxides that are not re-oxidised to nitric acid.

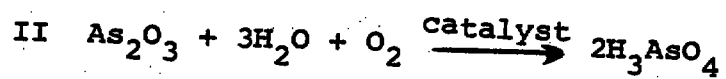
Nevertheless, despite all the problems mentioned above, the nitric acid method has for many years remained the generally accepted method for the manufacture of arsenic acid on an industrial scale.

The present invention provides a process for the manufacture of arsenic acid which comprises causing arsenic trioxide to react with water and oxygen in a sealed reactor at an elevated temperature and under a pressure of from 3 to 10 bar, in the presence of a catalyst comprising nitric acid in conjunction with iodine or an iodine compound, the nitric acid being present in an amount not exceeding 5% by weight, calculated as HNO_3 and based on the weight of arsenic trioxide.

It has surprisingly been found that, by means of the process according to the invention it is possible to overcome - in an industrial-scale process - many of the disadvantages of the conventional industrial process for the manufacture of arsenic acid, by the nitric acid method. Thus, in the process according to the invention, the foaming and attendant problems resulting from the evolution of the gaseous nitrogen oxides are avoided as also is the need for expensive nitric-acid-recovery apparatus. Another important advantage of the present process is that the need for large, stoichiometric (with respect to the arsenic trioxide) amounts of nitric acid is avoided. The present invention is thus considerably more economical than is the conventional process.

25 In the process according to the invention, arsenic trioxide is oxidised by water and oxygen in the presence

of a catalyst, and the overall reaction may be represented in simple form as follows:

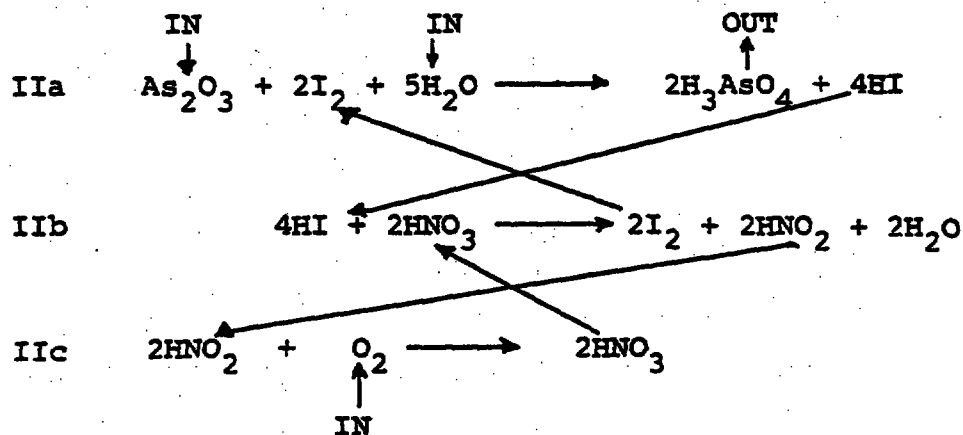


The catalyst used in the present process comprises

nitric acid and iodine or an iodine compound. The iodine compound may be any compound that will form iodide ions, for example, potassium iodide, hydriodic acid, or an iodate. Preferably, however, iodine (I₂) is used: if, for example, potassium iodide were used, the arsenic acid obtained at the end of the process would contain a small amount of potassium nitrate, which has been found difficult to remove.

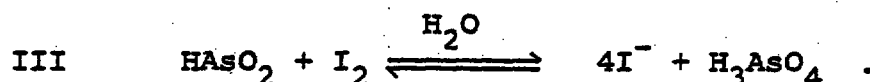
The amount of catalyst used is not generally critical, but it may depend on the other reaction conditions, and, moreover, it has been found that, at least in some cases, the rate of reaction can be controlled to some extent by varying the amount of catalyst used or the amount of one of the catalyst components.

It is thought that, when using a nitric acid/iodine catalyst, the reaction taking place in the process according to the invention in fact proceeds by a complicated series of reactions, which may be represented by the following simplified reaction scheme:



It will be seen that the sum of equations IIa, IIb and IIc is equation II shown previously.

It is also thought that the complicated reaction cycle involves, as one step, the equilibrium represented as follows:



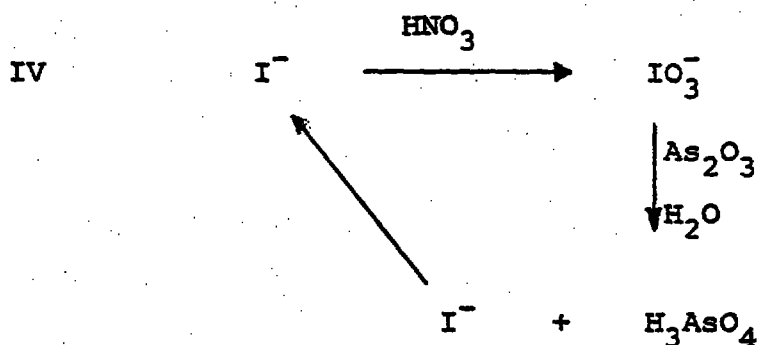
In order for the reaction cycle to proceed in the desired manner, as shown by equations IIa, IIb and IIc above, it is necessary for the equilibrium represented by equation III to be driven to the right-hand side.

It has been found that that can be achieved at a relatively high acid pH, but that a low pH favours the left-hand side of the equilibrium as shown. It is therefore important to the process of the invention that the amount of nitric acid present should not be such that the equilibrium shown above is prevented from proceeding to the right.

The conventional industrial process for the manufacture of arsenic acid, by the nitric acid method, uses a very large amount of nitric acid as mentioned previously and hence could not proceed through the reaction scheme shown above by equations IIa, IIb and IIc, because the equilibrium shown as equation III would be driven to the left-hand side. In fact, it is thought that the conventional nitric acid method, when using the conventional catalyst, potassium iodide, proceeds - in contrast to the present process - through a reaction cycle involving iodate, represented in simplified form as follows:

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In that reaction cycle, the iodide is regenerated and hence is a catalyst, but the nitric acid is consumed, by oxidation to nitrogen oxides as shown by equation I. In contrast thereto, in the present process, both the iodine or iodide and the nitric acid serve as catalysts.

It can be seen from equations IIa and IIb that there is a direct stoichiometric relationship between the amount of iodine or iodide and the amount of nitric acid that needs to be used. Thus, theoretically, only a minimal, catalytic, amount of nitric acid need be used: enough to initiate the reaction, because thereafter it will be continuously regenerated in situ as shown by equations IIb and IIc above. It has been found, however, that if too small an amount of nitric acid is used, the reaction stops prematurely, but can be restarted by the addition of more nitric acid. It is thought that this is because the nitric acid is slowly lost by reaction with impurities in the arsenic trioxide used and/or by reduction to

dinitrogen oxide N_2O by means of, for example, the arsenic trioxide and/or the iodide present, dinitrogen oxide being stable and not reacting with oxygen to give the higher oxides.

5 The nitric acid is, therefore, preferably used in excess of the stoichiometric amount with respect to the iodine or iodide, that is to say, the nitric acid is preferably used in an amount exceeding 0.5 mole per gram atom of iodine in the iodine or iodine
10 compound (see equation IIb above). It will, however, be appreciated from what has been said previously that the nitric acid must not be used in too great an excess, since otherwise the pH of the reaction mixture will become too low. The amount of nitric acid used does not
15 exceed 5%, and is preferably from 0.1% to 3% by weight, calculated as HNO_3 and based on the weight of arsenic trioxide used. Typically, from 20 to 60 litres of commercial nitric acid may be used per tonne of arsenic trioxide.

20 The nitric acid used in the present process may be introduced in the form of nitric acid of any convenient strength according to what is available. It may, for example, be introduced as fuming nitric acid, ordinary commercial nitric acid (about 62% strength by weight), or
25 any nitric acid solution down to about 1% strength (by weight). It is merely necessary to alter the amount of water added to the reactor according to the dilution of the nitric acid used.

It is an especial advantage of the present process that it is not necessary to use large amounts of nitric acid, unlike conventional processes, carried out by the nitric acid method, in which the nitric acid has to be used in approximately stoichiometric amounts with respect to the arsenic trioxide.

The amount of iodine or iodine compound used is not generally critical and, relative to the amount of arsenic trioxide, may be similar to the amount used in the conventional, nitric acid method. It has, however, been found that the rate of reaction, and hence the degree of exothermicity and the reaction duration, can be controlled easily and very satisfactorily by the amount of iodine or iodine compound used, because it appears that the reaction represented by equation IIa is the slowest of the three reactions in the reaction scheme: with smaller amounts of iodine or iodide compound, the reaction proceeds more slowly and less exothermically. The amount of iodine or iodine compound need not exceed 0.1% by weight, based on the weight of arsenic trioxide, and may be as low as 0.01% by weight. Amounts of from 0.02 to 0.05% by weight, based on the weight of the arsenic trioxide have been found to be suitable: typically, about 0.3 kg of potassium iodide or about 0.5 kg of iodine may be used per tonne of arsenic trioxide.

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The process according to the invention is carried out in a sealed reactor under a pressure of from 3 to 10 bar, especially with nothing being allowed to leave the reactor during the process, although additional
5 oxygen, and possibly other reactants, may be fed in periodically or continuously. It has been found that this method of carrying out the process of the present invention enables considerably smaller amounts of nitric acid to be used, down to about 1% by weight based on the amount
10 of arsenic trioxide used, or even lower.

When using a sealed reactor, the process may suitably be carried out by first introducing the non-gaseous reactants into the reactor. Air or, preferably, oxygen may then be introduced to the desired pressure,
15 optionally with initial venting to remove atmospheric nitrogen, thus helping to improve the rate of reaction. Preferably, the oxygen and the liquid mixture of the other reactants are stirred or otherwise agitated in the sealed vessel, because good agitation increases the amount
20 of gas/liquid contact, and thus the rate of reaction. The amount of gas/liquid contact can also be increased by, for example, using a wide, shallow vessel to give a large gas/liquid interface.

25 As indicated above, the oxygen is used under pressure, both because that has the advantage of forcing more oxygen into solution, and also because the reaction step

shown by equation IIc above has been found to be very pressure dependent. The process is carried out at pressures of from 3 to 10 bar (from 45 to 150 psi (pounds per square inch)); pressures of from 4 to 8 bar 5 (from 60 to 120 psi), are generally suitable when carrying out the process on an industrial scale.

As the reaction proceeds, oxygen is consumed and consequently the pressure within the reactor falls. The reaction will continue as long as there is sufficient oxygen 10 and other reactants present, but the rate of reaction will slow down as the pressure falls. Preferably, therefore, oxygen is introduced into the reactor continuously or periodically throughout the course of the process in

order to maintain the pressure at, or bring the pressure back to, the desired value. That may be done automatically, for example by means of a valve that opens to admit oxygen whenever the pressure
5 within the reactor falls to a certain predetermined value, or by controlling the amount of oxygen introduced to match the rate at which it is consumed.

It can be seen from the reaction scheme that one mole of oxygen is consumed per mole of arsenic
10 trioxide. Thus, 1 tonne of arsenic trioxide requires about 1.2×10^7 litres of oxygen (measured at standard temperature and pressure), which corresponds to about 1400 litres of liquid oxygen, although the oxygen is, of course, present in the reactor in excess.

15 The process is advantageously carried out at a temperature not below 80°C , preferably not below 85°C , and not higher than 150°C , especially at a temperature within the range of from 95 to 150°C .

It has been found that, if the temperature is initially
20 too low, the reaction might be reluctant to start, and that, if the temperature is too high, the reaction cycle shown by equations IIa to IIc above becomes hindered by other reactions. Advantageously, the
25 reaction mixture is initially heated to from 100 to 120°C , whereafter the temperature rises to about 140 to 150°C as a result of the exothermicity of the reaction. The reactor is then preferably cooled

so that the temperature falls back to a temperature of from 100 to 120°C, which may then be maintained until the reaction terminates. Generally, the exothermicity of the reaction is sufficient to maintain that temperature, but heating may sometimes be necessary in the later stages of the reaction.

During the course of the process, the progress of the reaction can be controlled to some extent by varying the pressure and the degree of agitation, because it appears that the rate of dissolution of oxygen is a slow rate-determining step, as is the reaction step represented by equation IIa, discussed previously. The degree of exothermicity can also be controlled in that way during the course of the process and it can be advantageous to include a thermally controlled oxygen-inlet valve to override the pressure-controlled valve, and to throttle or cut off the oxygen supply if the temperature of the reaction mixture should reach a certain predetermined value of, for example, 150°C, and then to increase or recommence the oxygen supply as the temperature falls.

The end of the reaction is indicated by a rapid increase in the rate of oxygen consumption followed by a sudden cessation of consumption. The rapid increase in the consumption rate probably occurs because the final reaction is that represented by equation IIc and, at that stage in the process, the slow reaction

represented by equation IIa has finished.

When the reaction has terminated, the pressure may be released, and that may generally be done safely without risk of a boil-over as the temperature of the reaction mixture will normally be below its boiling point at atmospheric pressure. The gas being released will be mainly oxygen, but, when a catalyst including nitric acid has been used, there will be some content of nitrogen oxides and the gas should therefore preferably be released through a scrubber, which may be simply a packed tower through which the gas is passed upward and released into the atmosphere, while caustic soda is being passed through in countercurrent. The type and size of scrubber and/or venting stack required may be dictated by local health and safety regulations, although it should be noted that the emission levels of nitrogen oxides are low.

The content of the reactor will, at this stage, be primarily arsenic acid and water, although there will normally also be a small content of nitric acid and iodine. The nitric acid may be removed by adding a small quantity of arsenic trioxide and/or, preferably, by blowing it off by bubbling air or oxygen through the mixture while maintaining it at about 80 to 90°C. The iodine is generally removed simultaneously, as may be seen by a change in the colour of the reaction mixture, depending on whether coloured impurities are present. In any case, the presence or absence of iodine can easily

be ascertained simply by shaking a sample with chloroform: the presence of iodine gives a blue colouration.

The arsenic acid may then be filtered to remove any excess arsenic trioxide remaining and any other impurities. Its concentration may be ascertained from its specific gravity, and it may be diluted with water to the required strength. Tests have shown that the nitrate content of the resulting arsenic acid is generally less than 0.02% by weight, although it can be reduced even further by prolonged blowing of air or oxygen through the mixture.

The present process may be used not only with pure arsenic trioxide but also with commercial low-grade arsenic trioxide. The use of low-grade starting material may require the use of slightly larger amounts of catalyst, for example iodine and nitric acid, than would otherwise be necessary and may also require the use of a reaction temperature nearer 120°C than 100°C and a slightly longer reaction but low-grade material can be successfully used in the present process without the disadvantages described previously that tend to occur when it is used in the conventional, nitric acid process. The use of low-grade material may result in some residue in the resulting arsenic acid, but that can generally be filtered off or, depending on the intended use of the arsenic acid, may even be left in

the final product. Alternatively, low-grade material may initially be purified by, for example, stirring with water and nitric acid or another acid (for example hydrochloric acid) depending on the types of impurity present, and heating for a short period, and then filtering. Thereafter, it may be reacted under conditions similar to those used for pure starting material.

The process according to the invention has a number of advantages over the conventional process for the manufacture of arsenic acid, by the nitric acid method. Problems such as boil-overs, blow-outs and other problems associated with foaming are substantially avoided even when using low-grade starting materials. The need for expensive nitric-acid-recovery plant is dispensed with, with consequent saving in the amount of caustic soda needed for scrubbing the effluent gases.

Moreover, the need to use large volumes of nitric acid is avoided, with consequent economic savings, savings in storage requirements, and reduction of health and safety risks. In fact, when using a nitric acid/iodine catalyst, the total amount of nitric acid used in the

present process (about 7.5 kg per tonne of arsenic trioxide) is substantially less than the amount of nitric acid lost (through conversion to dinitrogen oxide and in other ways) in the conventional process (which 5 can amount to about 10% of the total amount used, corresponding to a loss of about 80 kg per tonne of arsenic acid). Thus, not only is the need to use large amounts of nitric acid avoided, but also the overall net consumption of nitric acid is considerably reduced. The net consumption 10 may, if desired, be reduced still further by including a small nitric-acid-recovery apparatus for recovering the residual nitric acid blown off from the arsenic acid as nitrogen oxides, but any such apparatus need, of course, be on a much smaller scale than that used 15 in the conventional process. (In this respect, it is worthy of note that, under United Kingdom regulations, the conventional process is registerable both as an arsenic acid manufacturing process and as a nitric acid manufacturing process, whereas the process according to the invention does 20 not require to be registered as a nitric acid manufacturing process even when a small nitric-acid-recovery apparatus is included.)

The process according to the invention is further illustrated by means of the following examples:

Example 1

500 g of arsenic trioxide (fairly pure),
325 ml of water, 4 ml of fuming nitric acid (density
1.5 g.ml⁻³) and 150 mg potassium iodide were loaded
into a pressure vessel. Oxygen was then fed in
5 under a pressure of 50 psi (about 3.5 bar), the vessel
was vented in order to remove most of the atmospheric
nitrogen, and oxygen was again fed in, to a pressure
of about 100 psi (6.9 bar). The reaction mixture was
then slowly heated to about 100°C, with stirring, thus
10 causing the pressure to rise to about 125 psi (about
8.6 bar). At about 100°C, the reaction started
and the temperature of the reaction mixture rose
to about 145°C as a result of the exothermic nature
of the reaction, while the pressure fell as a result
15 of oxygen consumption. More oxygen was fed in each time
the pressure fell to about 100 psi, to bring the
pressure back to about 125 psi, and, after the initial
exothermic rise, the temperature was maintained at
about 100°C by cooling as necessary. The end of the
20 reaction was indicated by a sudden cessation of oxygen
consumption, after about 1 hour.

The vessel was then vented through a scrubber
(because of the small amounts of nitrogen oxides mixed
with the oxygen). No foaming was observed on venting.
25 A small amount of arsenic trioxide was then added to the

reaction mixture and air was bubbled through for about an hour, while maintaining a temperature of about 70 to 80°C, in order to remove the small amount of nitric acid. The original potassium iodide, now present as iodine, was also removed during this procedure, as was evident from the change in the colour of the product from pale yellow/brown to colourless. Some water was also lost during this procedure. The product was then filtered to remove the small excess of arsenic trioxide..

10 The product was arsenic acid in a concentration of about 83 to 85% by weight, with a specific gravity of 2.0 to 2.14. Water was added in order to dilute the arsenic acid to 80% by weight strength. A yield of about 820 g of 80% arsenic acid was obtained. That
15 corresponds to a yield of about 91.5% of the theoretical yield.

A test for nitrate, based on the colour reaction of α -naphthylamine, showed the arsenic acid to have a nitrate content of less than 0.02% by weight.

20 Example 2

200 g of commercially available arsenic trioxide (impurities reported as Fe 0.5%, Pb 0.5%, Cu 0.5%, Sb 1 to 1.5%, totalling 2.5 to 3%, or 3.5 to 4% on the assumption that the impurities are present as oxides;
25 darkish grey in colour, as compared with white, pure arsenic trioxide, but similar to pure sample in density and particle size), 130 ml of water, 3 to 4 ml

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of fuming nitric acid (see Example 1) and 50 mg of potassium iodide were loaded into a pressure vessel.

The procedure of Example 1 was followed, with the variations that the temperature was maintained at about 120°C instead of 100°C, and that the pressure was allowed to fluctuate between about 100 psi (about 6.9 bar) and 160 psi (about 11.0 bar) instead of between 100 and 125 psi.

80% by weight strength arsenic acid was obtained after a reaction time of about 4 hours. The product was covered with a fine black scum and also left a grey/black residue in the bottom of the reactor. The black scum sank in water and its colour suggested it could be elemental arsenic or antimony, which was confirmed by subsequent analysis. The total weight of impurities corresponded to about 3 to 4% by weight based on the arsenic trioxide.

This example shows that the present process works quite satisfactorily with crude commercially available arsenic trioxide, although the amount of catalyst may have to be increased slightly as compared with the amount necessary for a comparable amount of fairly pure arsenic trioxide. (Other experiments showed that the amounts of nitric acid and potassium iodide given above were the minimum amounts necessary to give a satisfactory reaction with this particular sample of arsenic trioxide, and that decreasing the amount of either or both of those reactants gave only a sluggish or no reaction. It is thought that

the impurities in the arsenic trioxide interfere with the iodine/nitric acid double catalytic cycle.)

Example 3

200 g of commercially available arsenic trioxide of the type used in Example 2 was purified in the following manner: enough water to form a thin slurry was added, followed by the addition of 3 ml of fuming nitric acid, after which the mixture was heated at 70°C for 30 minutes, filtered, washed with water to remove residual nitrates, and finally filtered again.

The procedure of Example 2 was repeated using the thus-purified arsenic trioxide, except that a temperature of only about 100°C was found to be sufficient.

80% by weight arsenic acid was obtained after a reaction time of only 1 to 2 hours. A small quantity of a very fine black residue was obtained, but it represented less than 0.01% of the arsenic trioxide and less than 0.006% of the arsenic acid, and it need not be separated off for certain uses of arsenic acid.

This example shows that initial simple purification of the crude arsenic trioxide enables the reaction to proceed much more quickly and readily with results similar to those obtained using fairly pure arsenic trioxide. (Other experiments showed that the amount of catalyst could be reduced in this case.)

Example 4

Using the apparatus shown diagrammatically in the accompanying drawing, 5000 parts by weight of arsenic trioxide, 1.6 parts by weight of potassium iodide (or 2.5 parts of iodine) and 3000 parts by weight of water are mixed to a slurry in a premix tank 10 equipped with a stirrer 12, a solids inlet 14 and a water inlet 16. The slurry is then transferred via pipe 18 to a jacketed pressure reactor having a capacity of 8000 litres. The transfer is effected by applying a vacuum to the gas outlet 22 with valves 24, 25 and 26 closed and valves 28 and 30 open. The contents of the reactor 20 is then heated, via the reactor jacket, to about 85°C, while being stirred by means of stirrer 32. With valve 26 open and valves 24, 25, 28 and 30 closed, oxygen is fed into the reactor 15 through pipe 33 until a pressure of about 20 psi (about 1.4 bar) prevails inside the reactor. 62% nitric acid is then added through pipe 35, with valve 25 open, and further oxygen is fed in to a pressure of about 120 psi (about 8.3 bar). The reaction commences and is allowed 20 to proceed for from 2.5 to 6 hours, while maintaining pressure between 60 and 120 psi (between about 4.1 and 8.3 bar) by adding further oxygen periodically or continuously but otherwise having all five valves 24, 25 26, 28 and 30 closed, and while maintaining a temperature 25 of from 100 to 150°C within the reactor by circulating cooling water through the reactor jacket. When the

reaction has terminated the pressure within the reactor 20 is released by opening valve 24 thus causing the gases to pass through pipe 34, up through a caustic scrubber 36 to neutralise nitrogen oxides, and then via pipe 38
5 to a stack (not shown), from where they are vented into the atmosphere. Meanwhile, air is blown into the reactor 20 via pipe 44 and valve 46 and through its liquid contents in order to remove the residual nitric acid, while the reactor is heated by passing steam through its
10 jacket. Finally, the liquid contents of the reactor, namely arsenic acid and water, is cooled by passing water through the reactor jacket, and is then let out through the pipe 40 by opening valve 42.

Claims

1. A process for the manufacture of arsenic acid which comprises causing arsenic trioxide to react with water and oxygen in a sealed reactor at an elevated temperature and under a pressure of from 3 to 10 bar, in the presence of a catalyst comprising nitric acid in conjunction with iodine or an iodine compound, the nitric acid being present in an amount not exceeding 5% by weight, calculated as HNO_3 and based on the weight of arsenic trioxide.
2. A process as claimed in claim 1, wherein the nitric acid is used in an amount of from 0.1 to 3% by weight, calculated as HNO_3 and based on the weight of arsenic trioxide.
3. A process as claimed in claim 1 or claim 2, wherein the nitric acid is used in an amount exceeding 0.5 mole per gram atom of iodine in the iodine or iodine compound.
4. A process as claimed in any one of claims 1 to 3, wherein the iodine or iodine compound is used in an amount of from 0.01 to 0.1% by weight, based on the weight of arsenic trioxide.
5. A process as claimed in claim 1, wherein the iodine or iodine compound is used in an amount of from 0.02 to 0.05% by weight, based on the weight of arsenic trioxide.



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6. A process as claimed in any one of claims 1 to 5, wherein the reaction is carried out under a pressure of from 4 to 8 bar.
7. A process as claimed in any one of claims 1 to 6, wherein the reaction is carried out at a temperature of at least 80°C.
8. A process as claimed in claim 7, wherein the reaction is carried out at a temperature of at least 85°C.
- 10 9. A process as claimed in claim 8, wherein the reaction is carried out at a temperature of from 95 to 150°C.
10. A process as claimed in claim 1, carried out substantially as described in any one of the examples herein.
11. Arsenic acid that has been manufactured by a process as claimed in any one of claims 1 to 10.
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