

[54] **PROCESS FOR INCREASING THE CORROSION RESISTANCE OF AUSTENITIC STAINLESS STEELS**

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[58] Field of Search260/555; 148/6.14, 6.35

[56]

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[57]

ABSTRACT

A process is described for enhancing the corrosion resistance of austenitic stainless steels which are exposed to solutions containing ammonium carbamate. The process involves exposing the surfaces of such stainless steel equipment, which are exposed to ammonium carbamate solutions during, e.g., the commercial manufacture of urea and melamine, to the corrosive effects of such solutions for a period of time to induce significant corrosion of such surfaces, followed by contacting said surfaces at a temperature of at least about 100° C for a period of time with an oxidizing agent.

8 Claims, No Drawings

PROCESS FOR INCREASING THE CORROSION RESISTANCE OF AUSTENITIC STAINLESS STEELS

This invention relates to a process for improving the corrosion resistance of austenitic stainless steels in contact with solutions containing ammonium carbamate. As is well known, ammonium carbamate containing solutions are formed, and require processing, during the preparation of urea from ammonia and carbon dioxide, and in the preparation of melamine from urea.

During the last two decades, apparatus for such commercial manufacture which has been fabricated with austenitic stainless steel liners on the surface thereof exposed to ammonium carbamate solutions has been employed. While hot ammonium carbamate solutions were long recognized as extremely corrosive, and as presenting one of the most difficult corrosion problems in the chemical industry, the control and minimization of corrosion of austenitic stainless steel materials exposed to the carbamate solutions was achieved by maintaining in such solutions the presence of a small amount of oxygen. This technique is disclosed in the Netherlands Pat. specification No. 77,361, and corresponding U.S. Pat. No. 2,727,069. While various materials had been proposed and applied for the purpose of controlling the corrosion problem, particularly in the manufacture of urea, e.g., such materials as lead, silver, zirconium, titanium, alloys of zirconium or titanium, and various rust-resistant steels, the possibility of using austenitic stainless steels, with oxygen protection, has been especially valuable because such steels are relatively inexpensive and do not offer serious problems in processing, welding, and fabricating of the equipment and apparatus.

Even so, however, it is also known that as the temperature of a solution containing ammonium carbamate in contact with stainless steel surfaces increases, the risk of corrosion of the apparatus becomes much greater, and once corrosion has started at any particular place in the apparatus, the rate at which such corrosion proceeds can become very high indeed. (Corrosion rate is here to be understood as measured by the decrease in the thickness of the material per unit time, e.g., as expressed in mm. per year). Further, when a solution containing hot ammonium carbamate is processed, particularly in operations where such a solution is heated for particular processing requirements, local, excessive heating of the heat-transfer walls of the apparatus can occur as a result of temporary deviation from specified or ideal technological conditions. For instance, such abnormally hot local situations within the equipment can be attended by phenomena of inducing boiling of the solution. In such a situation, the boiling phenomenon can cause all or part of the oxygen present in the liquid phase to be transferred into the vapor phase. When this occurs, it is possible that, at least temporarily, insufficient oxygen is present to prevent corrosion of the surface of the metal at the place or places in question. This can lead to severe local corrosion, which, if allowed to continue, will penetrate, or at least weaken, the adjacent wall of the apparatus employed.

When such a situation develops, of course, continued operation of the manufacturing plant is impossible, or at least dangerous, and plant shut-down is required for repair of the apparatus (even without regard to possible

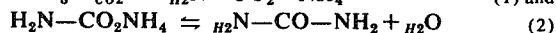
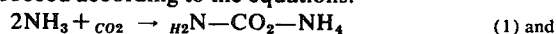
contamination of desired product with corrosion materials).

It is the object of this invention to improve the corrosion resistance of apparatus lined with austenitic stainless steels in contact with solutions containing ammonium carbamate, where the above-described circumstances can be further minimized even beyond that achieved by maintaining the presence of a small amount of oxygen in the reaction system.

More particularly, it is an object of this invention to provide a pre-treatment for the austenitic stainless steel metal surfaces used in such apparatus so that their resistance to corrosion during the processing operations is significantly enhanced.

The practice and nature of the present invention will be further understood in connection with a brief discussion of typical situations in which its usefulness is particularly valuable.

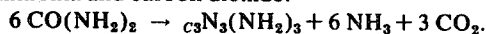
For instance, in the preparation of urea from ammonia and carbon dioxide, ammonium carbamate is first formed at a temperature of between about 170° C and 250° C, under a pressure of about 100 – 350 atm. This ammonium carbamate is then converted, subsequently or almost simultaneously, and possibly in the same vessel, into urea and water. These processes proceed according to the equations:



Reaction 2 is an equilibrium reaction and does not proceed to completion. The synthesis product leaving the urea autoclave, therefore, is a solution of urea in water, containing ammonium carbamate.

This synthesis solution, possibly after having been partially expanded, e.g., at reduced pressure, is subsequently heated to cause the ammonium carbamate present therein to decompose. Quantities of ammonia and carbon dioxide are thereby set free, and are separated from the rest of the solution. The balance of the solution is then treated in one or more (further) reduced pressure stages to remove the rest of the unconverted ammonium carbamate from the urea product solution. This heating and decomposition of carbamate can be carried out in several known ways, for instance, in a high pressure distilling column or in a so-called stripping column which is supplied with a stripping gas, which gas may be, for instance, one of the reaction components or an inert gas, such as synthesis gas for an ammonia synthesis, in order to expel ammonia and carbon dioxide present in the solution.

In another process, the preparation of melamine by the pyrolysis of urea is attended by the production of ammonia and carbon dioxide:



In known processes, after the melamine has been separated off, the ammonia and carbon dioxide stream mixture is treated in an absorption column. An aqueous solution of ammonium carbamate can then be obtained which is recycled to a urea synthesis.

It will be seen that in both of these processes, the processing of ammonium carbamate solutions is required, for the economics of the process. Further, such solutions of ammonium carbamate must be handled at relatively high temperatures, and under high pressures, as is well known in the art.

These liquid ammonium carbamate concentrated solutions in water, and aqueous urea solutions containing ammonium carbamate, are all very corrosive.

In the handling of such corrosive solutions localized high corrosion conditions can occur, as described above. This possibility is present in the use of apparatus wherein the surfaces exposed to such corrosion are fabricated from austenitic stainless steel, the alloy of which contains at least 16 percent chromium and at least 8 percent nickel, as well as other stainless steel alloys of even improved corrosion-resistant alloy composition.

In the past, the detrimental consequences of such localized corrosion of the useful lifetime of the equipment has been compensated for by employing greater corrosion allowances in the design of the equipment, i.e., by providing larger wall thicknesses, or thicker layers of the lining, for the equipment. Alternatively, materials having greater corrosion resistance in ammonium carbamate-containing media have also been employed in particular parts of the apparatus. However, it will be clear that both of these past approaches to solving such corrosion problems require appreciably higher plant investments and are undesirable for that reason.

While the relevant surfaces of the construction materials can be initially subjected to passivation treatments (and typically are in the manufacture of such apparatus), many experiments have established that the duration of the passive conditions achieved by normal passivation treatments is relatively small when the metals are exposed to solutions containing ammonium carbamate in which an insufficient amount of oxygen is present, as by the occurrence of the circumstances already described above. Such normal passivation treatments include the exposure of stainless steel surfaces to nitric acid, or mixtures of nitric acid and hydrogen fluoride.

Thus, while such typical passivation treatments of the stainless steels have no significant lasting effect, it has now been surprisingly found that the corrosion resistance of the austenitic stainless steel materials against ammonium carbamate solutions can be enhanced and maintained for appreciably longer periods of time, if these materials are first brought into a corroding solution by deliberate exposure in a non-protected way to ammonium carbamate solutions, and are then subsequently passivated at elevated temperatures with the relatively mild "passivating" agent of molecular oxygen itself.

More specifically, this invention relates to a process for increasing corrosion resistance of stainless steels, containing at least 16 percent chromium and at least 8 percent nickel against the corrosion normally experienced by contact of such materials with solutions containing ammonium carbamate.

The process according to the invention is characterized in that those surfaces of the austenitic stainless steel material, as will be in contact with said ammonium carbamate solutions, are first exposed for some time to the corroding action of such a solution in the substantial absence of oxygen and are then subsequently contacted at a temperature of at least about 100° C with a medium containing an oxidizing agent, said later contact being maintained for some time.

It has been found that when applying the second step in this method it is not necessary to use such powerful passivating agents, as the nitric acid or the mixture of nitric acid and hydrogen fluoride already mentioned. For instance, it is possible to make use of water which contains a small quantity of oxygen or an oxygen-emitting substance, such as hydrogen peroxide. Also, use can be made of a gaseous medium, such as air or carbon dioxide to which a small amount of air or oxygen has been added.

In effect, this invention provides a procedure for preparing the metal to be used in the contact with the corrosive ammonium carbamate solution, whereby the corrosion-preventive technique of processing such solutions in the presence of a small amount of oxygen becomes more effective over extended periods of time.

The process according to the invention can be applied to advantage, inter alia, in processes for the preparation of urea, in which the synthesis solution is subjected to the previously mentioned stripping treatment. This treatment is usually carried out at a very high pressure, preferably at synthesis pressure, so as to be able to effect the condensation of the expelled ammonia and carbon dioxide at a high as possible a temperature level without the intermediary of pumps or hot-gas compressors and, at the same time, to limit the quantity of water expelled together with these gases. This is done in view of the detrimental influence of water on the conversion in the reactor to which the gases expelled are recirculated after condensation. Even under the extreme conditions then prevailing, application of the measure according to the invention has been found to result in maintaining the passive condition of the material surfaces in question for appreciably longer times during a condition in which the supply of oxygen has become temporarily stagnant or is temporarily reduced to a value below the quantity required. The process according to the invention can also be applied in the preparation of melamine from urea, in which the ammonia and carbon dioxide set free are processed into an ammonium carbamate solution which is sent back to a urea synthesis stage.

The invention will now be explained in more detail with the aid of the following examples describing a few experiments conducted by applicant.

All of these experiments were carried out in such a way that mutually comparative results were rapidly obtained.

In view of this, urea synthesis solution was each time passed through a testing tube at a temperature which was considerably higher than the one usual in practice, while, also, no oxygen-containing stripping gas was supplied at all. The decomposition of the ammonium carbamate present in the solution and the expulsion of the liberated ammonia and carbon dioxide were effected purely thermically by supply of heat via the tube wall. The conditions, therefore, were purposely chosen in such a way that the occurrence of corrosion was strongly favored.

The occurrence of corrosion was established by judging the color of the urea synthesis solution flowing out of the testing tubes. For, when the material changes over from the passive into the corroding condition, the quantity of Fe dissolving per cm² and per time unit increases in very short time to such an extent that it

brings about a distinct discoloration of the solution. In addition to this visual judgement, the Fe contents of the urea synthesis solutions flowing in and out were determined periodically. The data thereby obtained confirmed, in all experiments, the visual judgments. Each time a distinct discoloration was established, a corrosion rate of between 40 and 60 mm/year was found.

EXAMPLE 1

A tube made in stainless steel of the composition 18 % of Cr, 12 % of Ni and 2.5 % of Mo was contacted, in the condition in which it was received from the supplier, (e.g., with normal nitric and passivation treatment) with a urea synthesis solution, while the external wall had a temperature of 210° C. The composition of the inlet solution was 30 % by weight of NH_3 , 20 % by weight of CO_2 , 40 % by weight of urea, the balance being water. The solution contained 5 ppm of oxygen, which corresponds to 0.5 % in the carbon dioxide supplied to the urea synthesis.

The tube started to corrode virtually immediately, at a rate of approximately 50 mm a year. This tube was then emptied and rinsed with water, whereupon air purge was applied for 12 hours at a temperature of 180° C. Subsequently with the same urea synthesis solution having the same oxygen content and at the same temperature as before the treatment, the corrosion rate was found to amount to only 0.05–0.1 mm a year after at least 250 hours, whereupon the test was concluded.

EXAMPLE 2

At a pressure of 125 atm a urea synthesis solution containing 5 ppm of oxygen was made to flow through a tube made of the above-mentioned 18-12-2 ½ Cr-NiMo-steel and being in the condition in which it had been delivered. The external wall of the tube was kept at a temperature of 230° C. Again, corrosion was found practically immediately. The corrosion rate amounted to 60 mm a year. This condition was maintained for 6 hours, following which the tube was emptied and flushed with water, whereupon, for 16 hours, a flow of carbon dioxide containing a small quantity of water vapor and 0.5 percent of oxygen by volume was passed through, the temperature of the external tube wall then amounting to 210° C. Next, the tube was subjected to a pressure of 125 atm. with the aid of carbon dioxide, following which urea synthesis solution was again passed through, while the temperature at the external wall of the tube again amounted to 230° C. Now corrosion was found only after 13 hours.

EXAMPLE 3

The experiment of Example 2 was repeated, now using air as passivating medium instead of carbon dioxide with water vapor and oxygen. In this test no corrosion was found for a period of over 50 hours.

EXAMPLE 4

The experiment of Example 2 was repeated once more, passivating now being effected for 16 hours, alternately with water and air. As from the moment the passing through of the urea synthesis solution was resumed, corrosion to a measurable extent was not found to occur for 53 hours.

EXAMPLE 5

In this case the tube was made of CrNiMo 25-25-2 Ti/stabilized steel. While the temperature of the external wall was kept at 230° C, a urea synthesis solution was again passed through this tube at a pressure of 125 atm. The inlet solution again contained 5 ppm of oxygen. Corrosion occurred within a few hours. This condition was maintained for 24 hours, following which the tube was emptied and rinsed with water. Next, the temperature of the external wall of the tube was adjusted to 210° C and flushing thereof was applied for 12 hours with carbon dioxide containing 0.5 percent by volume of oxygen and with water which flowed along the wall as a film. Upon completion of this treatment, the temperature of the external wall was again brought to 230° C and the supply of urea synthesis solution resumed. Corrosion was not found for 96 hours, whereupon the test was concluded.

The examples clearly show the favorable effect of the measure according to the invention on the resistance of austenitic stainless steels to corrosion in media containing ammonium carbamate. This effect is considerably higher under the milder conditions usual in practice, in which also a small quantity of oxygen is present which contributes to maintaining the passive condition of the material applied.

It is noted that the application of the process according to the invention is not limited to the treatment of new equipment, lines, etc. Also, the material of installations for the preparation of urea which have already been in operation can be successfully treated according to this process.

It will thus be seen that the practice of this invention involves exposing the surface of austenitic stainless steel, containing at least 16 % Cr and 8 % Ni to an aqueous corroding solution containing ammonium carbamate at elevated temperatures and under conditions and for a period of time sufficient to induce measurable, unacceptable corrosion of said surface, which if continued, would exhibit corrosion at a rate equivalent to at least about 25 mm/year, i.e., to induce corrosion of an amount equivalent to at least about 0.02 mm., or such that 10 mg. of Fe per cm^2 of corroded surface is dissolved in said solution, followed by contacting the thus-corroded surface at a temperature of at least about 100° C with an oxidizing agent of sufficient strength and for a required period of time sufficient to induce passivation of said surface such that measurable corrosion thereof upon re-exposure to said corroding solution and conditions will not be observed for at least about twice the period of time involved in said initial corroding operation.

It will be appreciated that the initial corrosion operation can be carried out at varying combinations of temperatures and periods of time, the significance being that this corrosion operation is conducted under such conditions which can be readily selected by those skilled in the art such that there is induced that degree of corrosion, if the conditions continued, which induces an unacceptable degree of corrosion which is here indicated as being at least about 25 mm. per year. Similarly, subsequent passivation operations may be conducted with various combinations of temperature and periods of time, the advantage of the invention

being indicated by the observation that after such passivation step the re-exposure of the corroded steel surface to the corroding operation will not exhibit such a measurable unacceptable corrosion rate for at least a period of time about twice the initial time involved in the initial corrosion.

What is claimed is:

1. A process for increasing the resistance of an austenitic stainless steel containing at least 16% of Cr and at least 8% of Ni against corrosion resulting from contact thereof with aqueous solutions containing ammonium carbamate, said process consisting essentially in that the surfaces of said steel is pre-treated by first exposing the same to an aqueous corroding solution containing ammonium carbamate at elevated temperatures and under conditions and for a period of time sufficient to induce a measurable corrosion of said surface which, if said conditions continued, would exhibit corrosion at a rate equivalent to at least about 25 mm per year, and thereafter contacting the thus-corroded surface at a temperature of at least about 100° C with an oxidizing agent of sufficient strength, said oxidizing agent selected from the group consisting of molecular oxygen and an oxygen emitting substance, for a required period of time sufficient to induce at least a

degree of passivation of said surface such that said measurable corrosion thereof upon reexposure to said corroding solution and conditions will not be observed for at least about twice the initial period of time involved in said initial operation of corrosion.

2. Process according to claim 1, wherein said oxidizing agent comprises water containing a small quantity of an oxygen-emitting substance.

3. Process according to claim 1, wherein said oxidizing agent is air.

4. Process according to claim 1, wherein said oxidizing agent contains a mixture of water and air.

5. Process according to claim 1, wherein said oxidizing agent comprises carbon dioxide containing a small quantity of oxygen.

6. Process according to claim 5, wherein said carbon dioxide also contains water.

7. Process according to claim 1, wherein said initial corroding operation is carried out under conditions such as to induce a corrosion rate of about 60 mm. per year, and for at least about 6 hours.

8. Process according to claim 1, wherein said initial corrosion operation is conducted at a temperature of at least about 175° C.

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