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PREVENTION OF CORROSION IN UREA SYNTHESIS

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This invention relates to the synthesis of urea by reaction of ammonia and carbon dioxide or compounds thereof and more particularly to the prevention of corrosion of apparatus employed for handling urea synthesis reaction mixtures.

It is known that when ammonia and carbon dioxide, or compounds of these substances with or without water, are heated in a closed system, a partial conversion to urea takes place. This general reaction has formed the basis of numerous patents and discussions in the literature directed toward a process for the commercial synthesis of urea. The reaction mixtures, which for convenience will be referred to as "urea synthesis melts" may vary widely in composition with varying proportions of reactants and/or with the extent to which the conversion to urea has taken place. The synthesis melts may contain, for example, various proportions of urea, ammonia, ammonium carbonates, ammonium carbamate, and water. The extremely corrosive nature of urea synthesis melts is known and a method has been proposed for the prevention of corrosion of chromium containing alloy steels in contact with these melts. In brief, this method consists in maintaining in the synthesis melt a small concentration of dissolved copper, which may be added in the form of the metal or any suitable compound, copper carbonate, or copper oxide, for instance. The amount of copper required is small, varying with the specific composition of the chromium alloy to be protected and being of the order of from about 0.03% to 0.3%. It is well known, however, that the vapor phase which may exist under some operating conditions over a urea synthesis melt is also corrosive though to a somewhat lesser extent than the melt proper.

We have found in practice that alloys which are somewhat resistant to attack in the liquid phase are so slowly attacked on those surfaces in contact with the vapor phase as to be serviceable for urea synthesis apparatus when protected from the liquid phase attack. Alloy steels which may be used in the above manner may vary widely in composition and we have employed among others (a) a steel containing 18% Cr, 8% Ni, and 2.5% Si; (b) a steel containing 18% Cr, 8% Ni, 1.5% Cu and 1.5% Mo; (c) a steel containing 18% Cr, 25% Ni and 3% Si. However, in view of the relatively expensive nature of the equipment required for urea synthesis it is highly desirable to avoid corrosion entirely or at least to minimize it wherever possible.

It is the object of the present invention to

provide a method of protection against vapor phase corrosion which will not only prolong the useful life of materials normally somewhat resistant to attack, but will also permit the use in contact with the vapor phase, of chromium-containing alloy steels which are rapidly attacked when unprotected.

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification in which its details and preferred embodiments are described.

Broadly speaking the invention consists in bathing or wetting, continuously or intermittently, the metallic surfaces exposed to vapors above the urea synthesis melt, with a liquid containing a non-volatile corrosion inhibitor dissolved therein. Thus, for example, when a vessel with inner surfaces of a chromium-containing alloy is employed in urea synthesis and the process is so operated that some surfaces are exposed to the vapor phase, corrosion of these latter surfaces is substantially inhibited by intermittently contacting them with a solution containing small amounts of copper. The solution employed may advantageously be the liquid phase of the reaction mass itself containing the necessary copper for protection. Other points of introduction of copper solution may be utilized, however. For example, if the process is of the continuous type the copper required for protection in the liquid phase may be introduced as a solution of cuprous ammonium carbonate at such a point as to first come in contact with the walls exposed to the vapor phase and thereafter pass into the liquid phase. Alternatively, pieces, strips or sheets of copper may be suspended in the vapor phase and in contact with the wall of the vessel so that by vapors condensing on the copper, the latter will be partially dissolved and the condensate containing dissolved copper will run down over the apparatus wall.

Another method of carrying out the present invention consists in maintaining in the liquid phase a concentration of copper and circulating a small proportion of the melt by means of a pump which discharges through a pipe so disposed as to jet the liquid against the surfaces which it is desired to protect.

The desired protection may more advantageously be secured, however, by the preferred method which consists in causing one or more of the gases involved in the synthesis to convey all or part of the liquid phase containing copper, so as to bring the liquid into contact with the

surfaces which would otherwise be exposed only to the vapor phase. For example, part of the carbon dioxide entering the autoclave may be directed through a central tube functioning as an "air lift" pump and causing part of the liquid phase to be ejected against the head of the autoclave.

The foregoing methods are given as examples only and other methods of contacting the liquid with the walls of the vessels employed will be readily apparent to those skilled in the art.

The frequency with which the walls exposed to the vapor phase are wet with the protecting liquid will depend in part upon the means chosen to effect the wetting. The greatest degree of protection will be obtained when the walls are constantly wetted. While it is preferable that the contacting periods should be so frequent as to approach continuity we have found that any wetting of the surfaces with a copper solution as hereinbefore described is beneficial.

As previously stated the copper employed in the present process may be introduced either as metallic copper or in the form of a suitable compound. It is to be understood, therefore, that reference to copper broadly in the appended claims is to be taken as including copper whether introduced in the free state or in chemical combination.

The present invention is not restricted in its applicability to the effecting of the synthesis reaction per se. If, for example, the separation of urea from unconverted raw materials and by-products is effected by distillation in a vessel separate from the reaction vessel, corrosion during the distillation may be prevented by employment of the general process hereinbefore described.

It will be understood that where reference is made in the specification or appended claims to the phrase "ammonia and carbon dioxide", said phrase shall be construed as covering ammonia and carbon dioxide as such or as compounds containing the same.

Various changes may be effected in the method and apparatus described without departing from the invention or sacrificing any of the advantages thereof.

We claim:

1. In the synthesis of urea involving the heating of ammonia and carbon dioxide in a metallic vessel the improvement which consists in protecting metallic surfaces exposed to the vapors above the synthesis melt by bathing said surfaces with a liquid containing dissolved copper.

2. In the synthesis of urea involving the heating of ammonia and carbon dioxide in a chromium steel vessel at elevated temperatures, the improvement which consists in protecting metallic surfaces exposed to the vapors above the synthesis melt by bathing said surfaces with a liquid containing dissolved copper.

3. In the synthesis of urea involving the heating of ammonia and carbon dioxide in a metallic vessel, the improvement which consists in protecting metallic surfaces exposed to the vapors above the synthesis melt by bathing said surfaces with a portion of the melt containing copper dissolved therein.

4. In the synthesis of urea involving the heating of ammonia and carbon dioxide in a chromium steel vessel, at elevated temperatures, the improvement which consists in protecting metallic surfaces exposed to the vapors above the synthesis melt by bathing said surfaces with a portion of the melt containing dissolved copper.

5. In the synthesis of urea involving the heating of ammonia and carbon dioxide in a chromium steel vessel at elevated temperatures, the improvement which consists in protecting metallic surfaces exposed to the vapors above the synthesis melt by substantially continuously circulating in contact with said surfaces a portion of the melt containing dissolved copper.

6. In the synthesis of urea by reaction of ammonia and carbon dioxide in a chromium steel vessel at elevated temperatures, the improvement which consists in continuously circulating into contact with metallic surfaces exposed to vapors above the melt a portion of said melt containing dissolved copper, by introducing one of the reactants in a gaseous state below the level of said melt.

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