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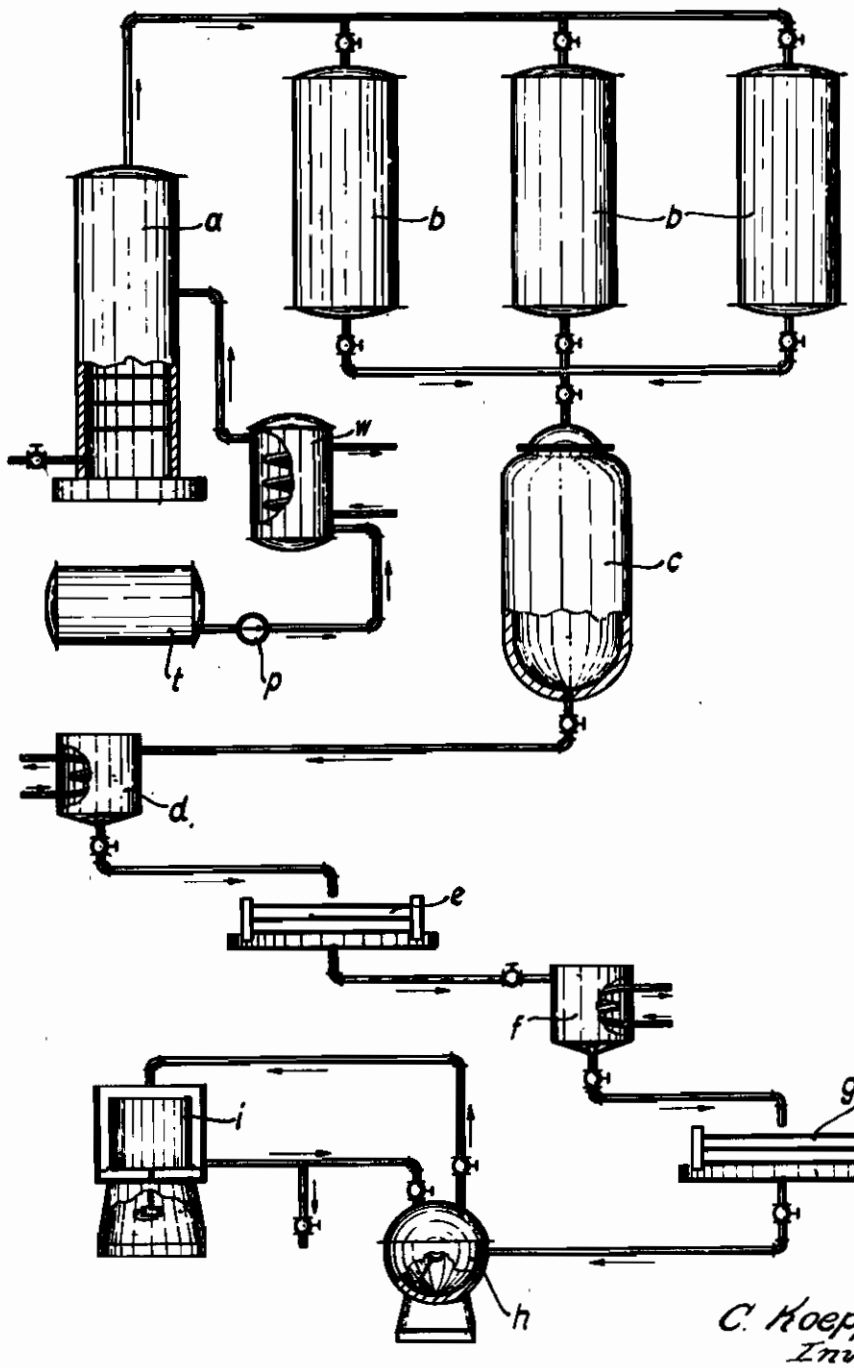

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METHOD AND APPARATUS FOR PRODUCING UREA

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It is known that urea ($CO(NH_2)_2$) may be produced synthetically by treating carbonic ammonia salts in autoclaves under pressure and at temperatures of about 150° C, the ammonia salts being charged into the autoclave either in solid or molten form. The ammonia salts forming the charging material for the urea synthesis may be produced in several ways, for instance, by vaporising under pressure a solution containing a high percentage of carbonate of ammonia

$$((NH_4)_2CO_3+H_2O)$$

or cabaminate of ammonia ($(NH_3)_2CO_2$), the resulting vapour-mixture, which consists of ammonia (NH_3), carbonic acid (CO_2) and some water, being passed into coolers in which the salts are precipitated either in the form of solids or as a molten mass. In order to produce urea the molten carbaminate is then transferred to the urea autoclaves for further treatment. Now, it has been discovered that this commonly practised and comparatively expensive production of the highly saturated solutions of carbonic ammonia salts, which have to be prepared separately from pure charging materials, may be avoided by using in their stead ordinary strong ammonia liquor, such as produced in coke oven plants, gas works or low-temperature carbonising plants, as starting solution. Strong ammonia liquor is a raw product obtained in coke oven plants, gas works, low-temperature carbonising plants etc. by condensing the vapours produced in distilling diluted gas washing liquids or the condensates of crude gases. In addition to about 20–25% ammonia (NH_3), which is its chief constituent, the strong ammonia liquor contains many impurities, such as carbonic acid (CO_2), hydrogen sulphide (H_2S), heavy and light hydrocarbon compounds, cyanogen (CN), sulphocyanogen (CNS), phenoles and their homologues etc.

Now, the invention consists in making this raw and impure strong ammonia liquor of varying composition usable as an advantageous charging material for the commercial urea synthesis without any considerable preliminary purification by adapting the known process for the production of urea to the impurities and the varying composition of the strong liquor.

The production of strong ammonia liquor is commonly preceded by the removal of acid from the weak liquor which is to be treated to produce strong liquor. For this purpose the weak liquor is heated to about 90 to 95° C in so-called deacidifiers and most of the carbonic acid and hydrogen sulphide contained in the weak liquor is thus removed, direct steam being added if necessary. Owing to the preliminary removal of acid from the weak liquor higher percentages of ammonia are attainable in the strong liquor. According to the invention the acid is incompletely removed from the strong ammonia liquor for the urea synthesis, i. e. the removal of acid is stopped prematurely, preferably after most of the hydrogen sulphide and a small part of the carbonic acid have been removed. Instead of operating with a reduced deacidification period the acid can also be removed from the weak liquor at low temperatures. The most favourable operating temperature for this incomplete removal of the acid is about 70 to 90° C. preferably 80° C±5°, according to the composition of the weak liquor and the quantity and nature of the steam which is introduced. The purpose of the incomplete deacidification is to pass most of the carbonic acid into the strong liquor for binding the ammonia in the form of carbaminate ($(NH_3)_2CO_2$) later on. It is advisable, however, to adjust the deacidification process in such a way as to obtain a deficiency of carbonic acid in relation to the quantity of carbonic acid which is stoicheiometrically required for binding the ammonia.

The strong ammonia liquor thus obtained is fed into a pressure vessel or—for further continuous treatment—into a second still. As no stoicheiometrically prepared solutions are available, but only impure weak liquor with varying carbonic acid, ammonia and hydrogen sulphide content, a method of operation which may be adapted to the varying content of absorbed gases and vapours is required for distilling the gases and vapours from the strong liquor under pressure. In order to obtain as high a yield of urea as possible, however, the object of distilling the gases and vapours from the strong ammonia liquor under pressure must be to obtain a solid or—if the cooling is slight—a molten salt with a nitrogen content as high as possible in the coolers for precipitating the carbonic ammonia salts, these coolers being arranged in succession to the still. The production of carbaminate

$$((NH_3)_2CO_2)$$

with as little carbonate of ammonia

$$((NH_4)_2CO_3+H_2O)$$

and bicarbonate of ammonia ($(NH_4)HCO_3$) as possible is therefore aimed at. In order to obtain almost pure carbaminate of ammonia ($(NH_3)_2CO_2$) strong ammonia liquor is, according to the invention, distilled under pressure, a surplus of ammonia being used in order to increase the partial pressure of the ammonia in the strong liquor to be charged and/or the pressure in the distilling apparatus being altered in accordance with the actual proportion of ammonia to carbonic acid, so that carbaminate of ammonia is the only stable compound in the apparatus, being precipitated in the coolers from the vapours. In practice the pressures to be maintained in the distilling apparatus range

from about 10 atm. gauge when there is little carbonic acid present to about 30 to 35 atm. gauge when there is a large surplus of carbonic acid. In this way solid or molten salts with 90 to 95% carbaminate of ammonia may without difficulty be continuously produced, superfluous carbonic acid as well as hydrogen sulphide (which has the highest vapour pressure), which may occasionally be present in the cooler, being simultaneously or separately blown off in a suitable manner. As ammonia may also escape in the removal of these gases the blown off gas is, according to the invention, furthermore returned to the crude gas current from the coke oven plant, gas works, low temperature carbonising plant etc. before it reaches the ammonia gas washers. Special washing devices arranged in succession to the distilling apparatus for recovering the ammonia may thus be dispensed with. All the above measures and operations are therefore not necessary in every case in order to obtain ammonia salts with a high carbaminate content. The blowing off of the residual acids may therefore be dispensed with according to the nature of the strong liquor used, though its retention appears advisable owing to the fact that residual gases which are not combined with ammonia will slow down the formation of carbaminate and consequently reduce the yield of the plant. Most of the impurities of the strong liquor mentioned at the beginning of this description remain in the water discharged from the strong liquor still. In addition the discharged water contains a residue of ammonia and carbonic acid, the quantities of which depend upon the equilibrium of absorption and the partial pressures of these gases and vapours in the presence of water at various temperatures and under different pressures. According to this invention this water discharged from the strong liquor still is returned to the weak liquor still, in which the residue of utilisable gases and vapours is removed.

The method according to the invention is further explained by the example of a plant shown in the diagram.

In this plant shown as an example the strong ammonia liquor is charged into the still *a* and the resulting gases or vapours passed into the coolers *b* arranged in succession to the still for precipitating or condensing the carbonic ammonia salts in solid or—if the cooling is slight—in molten form, the object being to obtain as high a nitrogen content as possible, i. e. the production of carbaminate of ammonia ($(NH_3)_2CO_2$) with a minimum content of carbonate of ammonia ($(NH_4)_2CO_3+H_2O$) and bicarbonate of ammonia ($(NH_4)HCO_3$). Following its production the carbaminate is transferred to the urea autoclave c in which urea is produced in the known manner. After the partial conversion of the carbaminate ($(NH_3)_2CO_2$) into urea ($(NH_2)_2CO$) the salts of ammonia which are not converted are distilled over—also in the known manner—into a pressure vessel in which a lower temperature is maintained. Whereas special pressure-resisting receivers have been used up to the present for precipitating the resultant mixture of ammonia and carbonic acid gases and vapours in the form of ammonia carbaminate, to which is added a large part of the hydrogen sulphide which enters the autoclave with the carbaminate, it has been found that these residual gases and vapours are very much more easily and cheaply precipitated in the coolers *b* arranged in succession to the strong liquor still for producing carbaminate. In addition to the impurities carried along in the process, i. e. mainly sulphide of ammonium (NH_4SH), small quantities of hydrocarbon compounds and cyanogen compounds the urea solution leaving the autoclave *c* after having been thickened in the manner described above contains fresh impurities in the form of metallic sulphides, metallic oxides and thiourea ($(NH_2)_2CS$). Apart from these there are always also residual ammonia and residual carbonic acid in the watery urea solution. Whereas up to the present the residual gases and vapours separated from the urea solution were recovered in washers arranged in succession to the process, coke oven plants, gas works, low-temperature carbonising plants can, according to the invention, dispense with a separate secondary washer for waste vapours from the thickening pans *d*, which contain ammonia, carbonic acid and hydrogen sulphide by returning these waste vapours to the crude gas stream before it reaches the ammonia washers. It has further been found that the above-mentioned solid impurities, with the exception of the thiourea, may be removed almost completely from the watery urea solution by diluting the watery urea solution before it is thickened in the pan or pans *d* with a large quantity of water and then thickening it. As the diluted solution boils longer during the thickening the oxidiferous and sulphurated impurities assume a flaky form. In a diluted solution these flakes settle better than in viscous urea solutions and are accordingly more easily filtered. In addition they practically retain the whole of the hydrocarbon residues which are often present on the filter *e*. According to the invention it is advisable to thicken the urea solution (or melt) leaving the urea autoclave *c* in two stages by filtering off the impurities, which are converted into an easily filterable state by boiling up the diluted urea solution, after the last traces of ammonia and carbonic acid have been distilled off. This also ensures a saving in the oxidising agents to be added in the next operation.

The final operation consists of removing, according to the invention, the small quantities of thiourea contained in the solution by oxidation in the pan *f*. Dioxide of manganese (MnO_2), hydrogen peroxide (H_2O_2) and other known oxides are particularly suitable as oxidising agents. Hydrogen peroxide (H_2O_2) has the advantage of being free from residue. Moreover, by the addition of the oxidising agent any residual quantities of metallic oxides and metallic sulphides are, if necessary, converted into a very easily filterable form, so that a second filtration through filter *g* leaves a light and clear urea solution, which merely requires thickening to produce pure urea. The urea solution is thickened in the crystallising pan *h*, from which the urea is passed to a centrifuge *i*. The residual liquid discharged from the centrifuge *i* is returned to the crystallising pan *h* in order to recover the remaining particles of urea which are discharged in this water.

t is the collecting container for strong liquor, *p* the pump for strong liquor and *w* the preheater for preheating the strong liquor. The preheaters *w* and the pans *d* and *f* may be heated by heat exchange by utilising the waste heat of the process.

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