

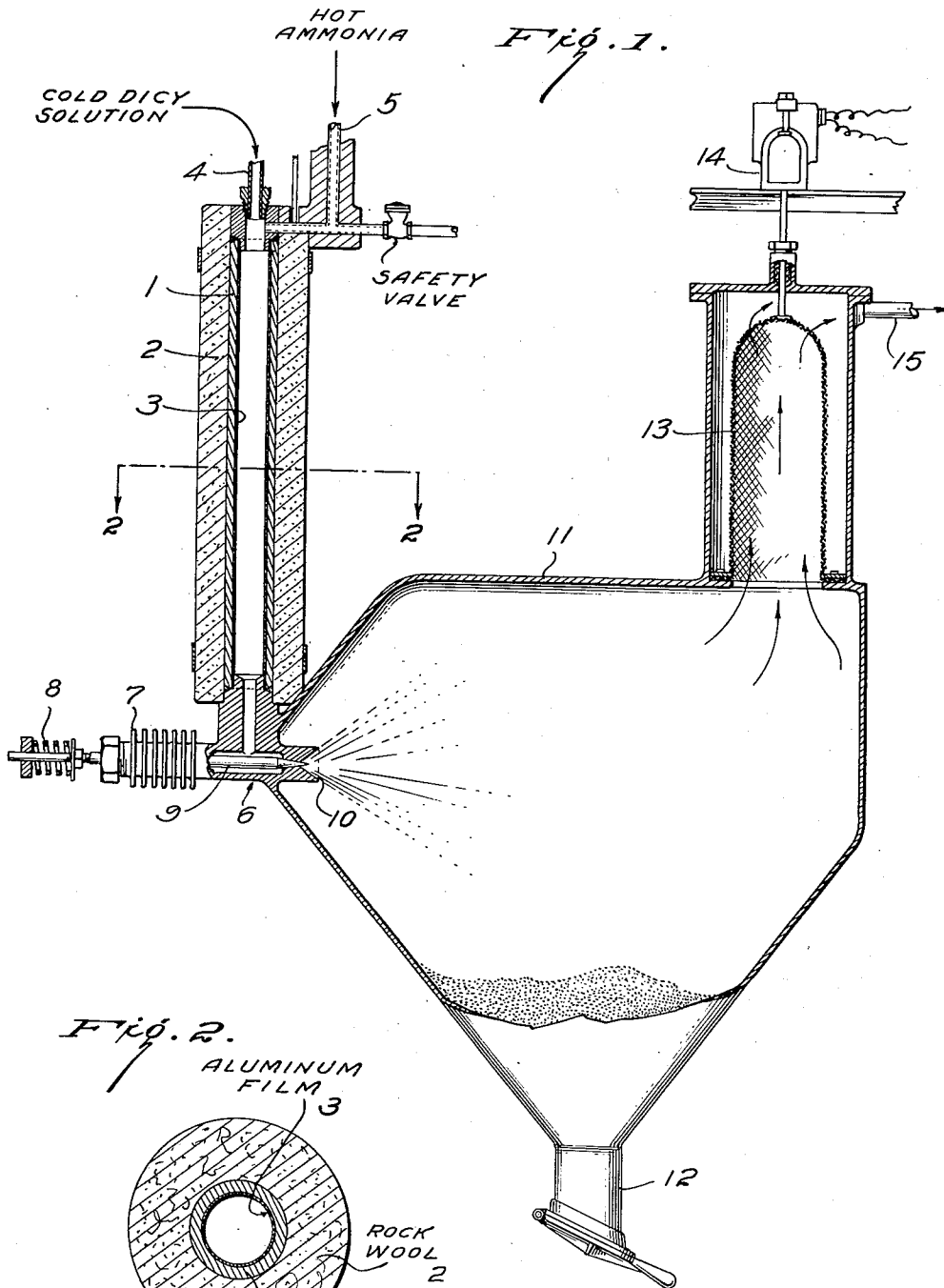
Nov. 20, 1951

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PRODUCTION OF MELAMINE

2,575,498

Filed March 26, 1951

2 SHEETS—SHEET 1



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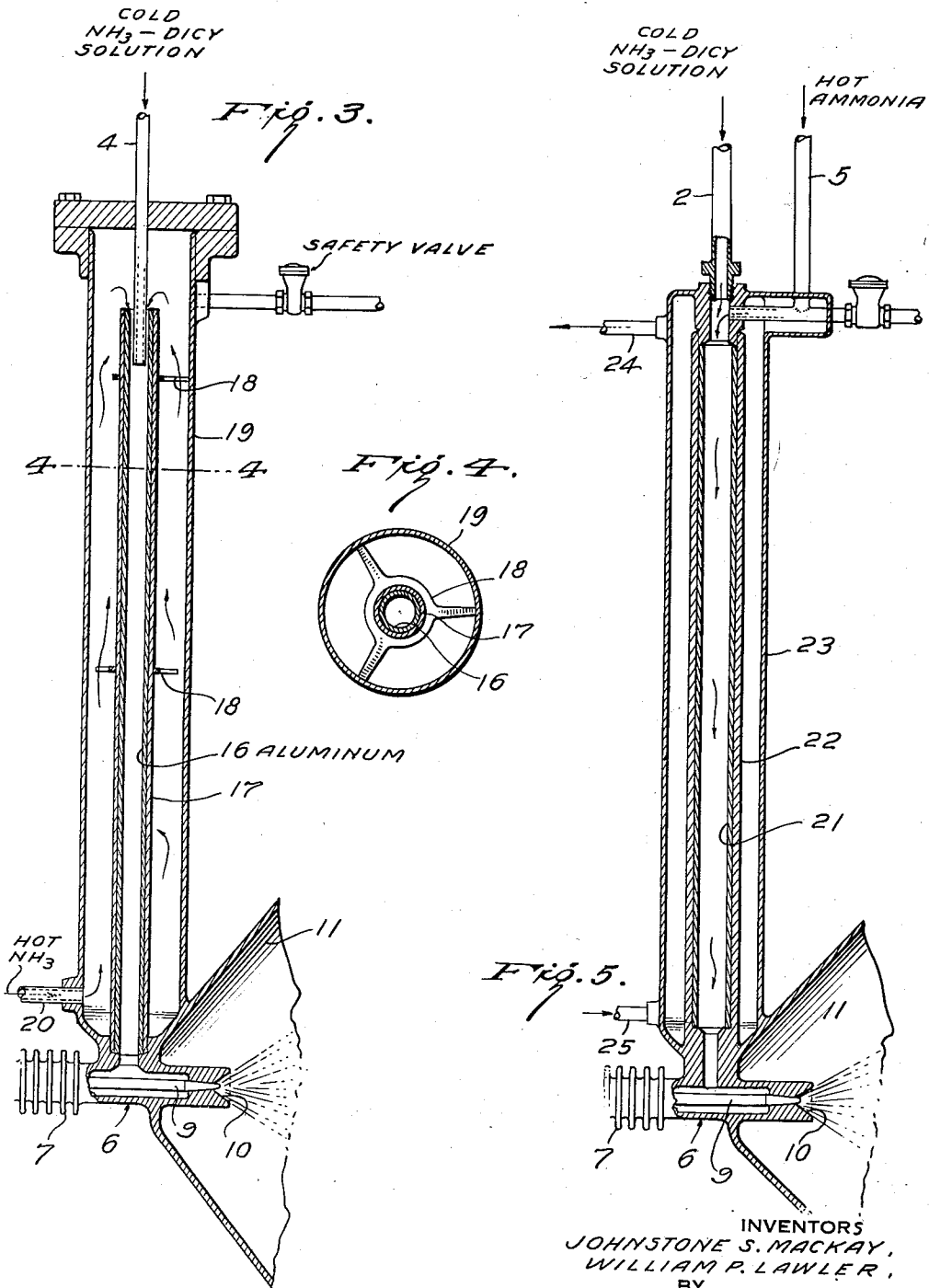
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UNITED STATES PATENT OFFICE

2,575,498

PRODUCTION OF MELAMINE

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5 Claims. (Cl. 260—249.7)

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This invention relates to an improvement in the art of preparing melamine, and more particularly to the preparation of melamine in a high temperature reaction tube.

The high temperature method of making melamine is an important one, but suffers from the disadvantage that the melamine-forming material, such as dicyandiamide, urea, or the like, generally dissolved in liquid ammonia, tends to corrode the interior of the reaction tube at the high temperatures necessary to form melamine by this method, resulting in a short life of the reaction tube and impurities in the melamine produced. In the high temperature processes, it is normal to use temperatures within the range 350°–600° C. and ammonia pressures of 100–10,000 p. s. i., or even higher. Under such stringent conditions the attack on the lining of the reaction tubes usually employed is severe. For example, it has been found that reaction tubes of stainless steel, platinum, and silver, are quickly corroded and that non-metallic surfaces such as borosilicate glass, ceramic liners, and glazed metals, are corrosion resistant but fail owing to thermal shock.

It is an object of this invention to provide a reaction tube for melamine production more suitable than those heretofore used. It is a further object to provide a more durable reaction tube relatively free from corrosion and shock under the conditions obtaining in high temperature processes for making melamine. It is a still further object to provide a rapid and continuous process for making a high-purity melamine.

It has been found that a liner consisting of aluminum metal may be used to contain the reaction, and that the liner so used is resistant to both corrosion and thermal shock. The aluminum lining is preferably prepared by hot-dipping a stainless steel tube in molten aluminum metal, but it can also be prepared by spraying molten aluminum into a tube of stainless steel or other high temperature resistant metal in such a way that the interior of the tube is covered with aluminum metal spray. The aluminum coating may also be deposited by evaporating molten aluminum in a vacuum and permitting the vapor to condense on the interior of a tube of metal that is structurally strong at high temperatures. Another method of forming the liner is to draw a stainless steel pipe (or other high temperature resistant metal or alloy such as aluminum bronze) down over an aluminum pipe. A still further method is to machine an aluminum tube to a predetermined outside di-

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mension, and to swage a supporting tube of metal resistant to high temperatures over the thus machined aluminum tube.

Among the advantages that result from the use of an aluminum reaction tube liner two stand out, namely, much longer runs between shut-downs for repairs to the reaction tube, and production of a purer grade of melamine.

To describe the invention in greater particularity, reference is made to the accompanying drawings.

Fig. 1 is a side elevation, with parts cut away, showing an aluminum-lined reaction tube with accessory apparatus for making melamine.

Fig. 2 shows a cross section along the line 2—2 of the reaction tube of Fig. 1.

Fig. 3 is a side elevation showing an additional embodiment of the reaction tube, involving its external and internal heating by hot ammonia.

Fig. 4 shows a cross section along the line 4—4 of the tube assembly of Fig. 3.

Fig. 5 is a side elevation of a further embodiment of the reaction tube that permits either external or internal heating or both.

In Fig. 1 is shown a tube 1 of steel or other metal resistant to high temperature and pressure surrounded by insulation 2 such as rock wool or the like. Tube 1 is coated with a thin film of aluminum 3 and is connected to entrance ducts 4 for the cold melamine-forming solution, and 5 for hot ammonia. The lower terminus of the tube assembly comprises a pressure release valve shown generally at 6, which is equipped with the conventional Sylphon 7 controlled by spring 8, which is adjustable to cause valve stem 9 to unseat at any predetermined pressure, and thus to permit melamine vapor to be sprayed through valve orifice 10 into melamine collecting chamber 11, which is equipped with solids discharge gate 12 and gaseous discharge assembly comprising bag filter 13 agitated by vibrating means 14. The filtered gases are drawn off through tube 15 for storage or recycling.

In Fig. 3 an aluminum tube of substantial thickness is shown at 16, supported by a high temperature resistant tube 17 made of stainless steel or the like positioned axially by means of spiders 18 or the like within a containing chamber 19 of stainless steel or the like. Hot ammonia enters the system at 20, and heats the reaction tube on the outside as it rises, and then heats the cold ammonia-dicyandiamide (or other melamine-forming material) entering at 4 and converts it to melamine vapor during passage of the materials through the aluminum reaction

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tube 16. The melamine vapor is sprayed through valve 6 into hopper 11 with its various accessories as shown in Fig. 1.

In Fig. 5 there is shown an aluminum tube 21 supported by a high temperature resistant tube 22 such as stainless steel or the like contained axially within chamber 23 equipped with ports 24 and 25 for the passage of high temperature heat exchange media such as lead alloys and the like, for exterior heating of the reaction tube assembly 21 and 22. An entry for the melamine-forming material is provided at 2 and an entry for hot ammonia is at 5 for interior heating of the reaction tube. Thus either exterior or interior heating, or a combination of the two can be used, as desired. As in Figs. 1 and 3, melamine vapor is formed in and swept through the tube, and then sprayed through valve 6 into chamber 11.

The process will now be described in more detail, with particular reference to Fig. 1, which represents a preferred embodiment of the invention.

In using the aluminum reaction tube shown in Fig. 1, ammonia and a substance which forms melamine when heated, such as dicyandiamide, is passed through inlet pipe 4 into tube 1, along with hot ammonia introduced through pipe 5. The ammonia is heated by means of a pre-heater (not shown) to a temperature within the range 450°-600° C., and serves to heat the melamine-forming substance to a temperature at which melamine is formed. This hot ammonia passes through the reaction zone 3, and when the zone reaches optimum operating temperature (about 500° C.) a stream of cold, 50% dicyandiamide-ammonia solution is pumped through inlet 4, where it mixes with the hot ammonia from inlet 5. The solution entering through pipe 4 is held at a pressure of about 2000 p. s. i. The proportions of 50% dicyandiamide-ammonia solution and preheated ammonia are adjusted so that the resultant mixture contains about 15% dicyandiamide at the entrance of tube 3. The rate of feed is adjusted so that the reactants have a residence time of at least about 7 seconds within reaction tube 3. The melamine so produced together with excess ammonia is vented from the end of the reaction tube 3 through pressure regulated valve 6 and sprayed into receiving chamber 11. Exit temperatures of this mixture range from 400°-450° C., and it is important to maintain the exit temperature above the freeze-up point of valve 6, which is generally found to be about 370° C. Exit temperatures are easily regulated by regulating the entrance temperature of liquid ammonia into duct 5. For such purposes an entrance temperature for said preheated ammonia of 500°-600° C. ordinarily suffices. As the mixture of melamine and ammonia enters the receiving chamber 11 through orifice 10 the ammonia expands immediately and the resultant cooling effect causes the melamine vapor to pass quickly to the solid state so that it falls to bottom of the receiver as an extremely fine light powder.

Dicyandiamide is a preferred melamine-forming substance because of the speed with which it is converted into melamine under the conditions of this process. However, various other melamine-forming materials, such as urea may be used instead. If urea is used, the reaction tube should be somewhat longer, inasmuch as the conversion of urea to melamine requires a longer period of time. Still other melamine-forming substances that may be used include cyanamide,

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guanylurea, cyanourea, biuret, guanidine and its salts, cyanuric acid, ammelide, ammeline, melam, melem, melon, and others well known in the art.

The length and diameter of the aluminum-lined reaction tube obviously vary with the nature of the melamine-forming substance and the required capacity of the plant. When using melamine-forming substances that are almost instantly converted into melamine at the high temperatures of the process, such as dicyandiamide, the tube may be rather short; one successful conversion tube and its aluminum liner were only thirty inches long. The tube may be much longer, however, since melamine vapors are quite stable under the conditions of the process. When using urea, melam, and other substances that form melamine more slowly at the higher temperatures, the tube and aluminum liner may be longer than a comparable tube suitable for dicyandiamide, or the rate at which the former materials are passed through it may be slower.

When using dicyandiamide or other melamine-forming substances that are rapidly converted to melamine at temperatures of the process, it has been found that a vertical tube is preferable, as there is less danger of plugging the tube with solid melamine. When using urea as the melamine-forming substance, or other materials that form melamine more slowly than dicyandiamide or at higher temperatures, the reaction tube may be positioned horizontally or placed at an angle to the plane of the floor.

The following is an example using dicyandiamide in the apparatus of Fig. 3. The aluminum liner 16 was 1½ inches, inner diameter, x 7 feet long, and ¾ inch thick, supported by a stainless steel cylinder of similar length and about ¾ inch thick. Liquid ammonia preheated to about 550° C. was pumped into inlet tube 20. This hot ammonia passed up over the top of the liner and down into the reaction zone. When the reaction zone had reached operating temperature (about 500° C.) a stream of cold, 50% dicyandiamide-ammonia solution was pumped through inlet 4, where it mixed with the hot ammonia. The solution entering through pipe 4 was held at a pressure of about 2000 p. s. i. The proportions of 50% dicyandiamide and preheated ammonia were so adjusted that the resultant mixture contained 25% dicyandiamide at the top of the reaction zone. The rate of feed was adjusted so that the reactants had a residence time of 25-75 seconds within the reaction tube 16. The melamine and excess ammonia were vented from the end of the reaction tube through pressure-regulated valve 6 and sprayed into receiving chamber 11. Here the ammonia expanded immediately and the resultant cooling effect caused the melamine vapor to pass with extreme rapidity to the solid state so that it fell to the bottom of the receiver as an extremely fine light powder. Exit temperatures were of the order 400-450° C.

The following is an example using dicyandiamide in the apparatus of Fig. 5. Ammonia preheated to about 550° C. was pumped into inlet tube 5, thence into aluminum liner 21 and out through valve 6. The aluminum liner 21 consisted of a 4½ foot length of standard ¾ inch aluminum pipe, and was supported by an exterior steel shell 22, consisting of ¾ inch stainless steel pipe. When the temperature within the aluminum reaction zone 21 reached operating temperature (about 500° C.), a stream of dicyandiamide, dissolved in liquid ammonia in the

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weight ratio of about 1 part dicyandiamide to 1 part ammonia, was pumped into inlet tube at such a rate that the weight ratio of dicyandiamide to the total ammonia in reaction tube was about 1 to 3. Equilibrium pressure within the tube 21 was maintained at about 2000 p. s. i. The average retention time of material within the reaction zone was about 7 seconds. Recovery was approximately 97%-98% of theoretical, and the purity of melamine so produced was about 98.7%.

When it is desired to supplement heat provided by the pre-heated ammonia, a heat exchange medium such as a lead alloy is passed through heat jacket 23 with its ports 24 and 25. 15

The preferred temperature range for operating the invention is 350°-500° C. and the preferred pressure range 750-5000 p. s. i., and still more preferably, about 2000 p. s. i.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto but is to be construed broadly and restricted solely by the scope of the appended claims. 20

This is a continuation-in-part of applicants' co-pending Serial No. 81,450, filed March 15, 1941, now abandoned. 25

We claim:

1. In the process of making melamine comprising continuously passing a melamine-forming substance through a reaction zone in a tube maintained at a temperature within the 30

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approximate range of 350°-600° C., and under a pressure of at least 100 p. s. i., the improvement which comprises passing said melamine-forming substance through a tube the inner surface of which is aluminum. 5

2. The process according to claim 1 in which the melamine-forming substance is dicyandiamide and the pressure is ammonia pressure.

3. The process according to claim 1 in which the melamine-forming substance is urea and the pressure is ammonia pressure. 10

4. In the process of making melamine comprising continuously passing dicyandiamide through a reaction zone in a tube maintained at a temperature within the approximate range of 350°-600° C., and under a pressure within the approximate range 750-2000 lb./sq. in., the improvement which comprises passing said dicyandiamide through a tube the inner surface of which is aluminum. 15

5. In the process of making melamine comprising continuously passing urea through a reaction zone in a tube maintained at a temperature within the approximate range of 350°-600° C., and under a pressure within the approximate range 750-2000 lb./sq. in., the improvement which comprises passing said urea through a tube the inner surface of which is aluminum. 25

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No references cited.