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PROCESS FOR REACTING AMMONIUM NITRATE TO FORM NITROUS OXIDE

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This invention relates to the manufacture of nitrous oxide by the heating of ammonium nitrate to its temperature of decomposition and more particularly to such a process in which improvement in yield, purity and uniformity of gas development is obtained.

The commercial methods of the prior art for the manufacture of nitrous oxide have generally comprised the heating of ammonium nitrate to its decomposition temperature, with the resulting formation of gaseous nitrous oxide and water, according to the equation:

$$NH_4NO_3 = N_2O + 2H_2O$$

While the chemistry of this process is simple, the method of operation must be controlled very carefully for several reasons. Since the principal demand for nitrous oxide gas is as an anaesthetic, it is essential that a high purity product be obtained. A highly important consideration is that the reaction proceed smoothly. Since the decomposition reaction involves the conversion of a solid to gaseous products, a very great increase in volume occurs and an uncontrolled reaction might therefore become explosive in its effects. This control of the reaction velocity is important not only from a safety point of view but from the practical consideration of yield. The purity of the product is likewise dependent on the even course of the reaction, since, under some conditions of decomposition, nitrogen gas may occur as a product.

Nitrous oxide has been produced according to prior art practise by both batch and continuous processes, though the former has been most generally followed. One frequently practised method of operation has comprised the introduction of a considerable amount of ammonium nitrate, for example 600 pounds, into a retort vessel, either in solid lump form or as molten material. Heat has then been applied until the charge has been raised to the decomposition temperature, for example 240–260° C. Since the reaction is exothermic, no further application of heat is ordinarily necessary when once it has started. A certain amount of cooling may be desirable from this point on, in order to exercise the desired control over the decomposition velocity. Nitrous oxide is thus obtained as a decomposition product, together with water, which latter material may be largely removed by condensation.

Some of the processes of the prior art have controlled the reaction to a certain extent by dilution of the ammonium nitrate with inert materials, and the same effect has been obtained by utilizing as starting materials a mixture of salts in which ammonium nitrate is formed by double decomposition, for example sodium or potassium nitrate with ammonium sulfate. The most desirable method of procedure, however, has been found to be the use of pure ammonium nitrate by itself, the process being stopped when a predetermined amount of decomposition has occurred, 60 to 80% for example. Following such a procedure, a residue of 40 to 20% of the original ammonium nitrate is left in the retort, and sufficient fresh material can be added to bring the amount to the original quantity. Upon heating, renewed conversion to nitrous oxide will again occur. In this manner a succession of batch conversions can be carried out with the necessity of complete recharging of the apparatus only after considerable periods of time.

In the production of nitrous oxide from ammonium nitrate by the methods outlined, particularly where the reactor holds several hundred pounds of ammonium nitrate, the velocity of the reaction occasionally increases suddenly, and unexpected semi-explosive increases in gas evolution may take place. Such occurrences are due to an increase in reaction rate, and are generally accompanied by an increase in side reactions which give such undesirable products as ammonia, nitric acid and higher oxides of nitrogen, or nitrogen itself. Aside from the effect of local overheating, there is no general agreement as to the reasons for the occurrence of violent reactions. It seems probable, however, that the presence of certain impurities in small amounts in the reaction material might exert an undesirable catalytic effect on the various side reactions. If the operations are conducted in such a way that fresh ammonium nitrate is periodically added to the residual material from a previous batch operation, it is apparent that any non-volatile impurity that is deleterious to the smooth decomposition to nitrous oxide will increase progressively in amount present as successive operations are carried out.

While safeguards are maintained against such contingencies in the way of rapid cooling, pressure vents and releasable lids, so that there is little danger to life or permanent equipment, considerable loss in yield and reduction in gas purity result and the desired smooth operation of the method is interrupted.

The object of our invention is an improved process for the production of nitrous oxide by the thermal decomposition of ammonium nitrate. A further object is such a process wherein the

combined advantages are obtained of increased purity of product, improved yield, and a more uniform velocity of gas development. A still further object is a new composition of matter comprising ammonium nitrate particularly adapted for the production of nitrous oxide. Additional objects will be disclosed as our invention is hereinafter more fully described.

We have discovered that the foregoing objects are accomplished by maintaining in contact with the ammonium nitrate during the decomposition period a compound which not only increases the rate of decomposition of ammonium nitrate to N_2O, but also inhibits the side reactions which produce nitrogen and other impurities. Compounds of this type may be regarded as catalysts for the main reaction and inhibitors of the side reactions involved in the thermal decomposition of ammonium nitrate to N_2O.

A great many compounds are available which are suitable for the purpose of our invention. We have found, however, that materials comprising phosphorus and arsenic are especially effective. Preferably, but not necessarily, the elements should be a constituent of an acid radical and in general, while water-insoluble compounds of the elements mentioned give favorable results, we prefer to employ water-soluble materials. Since it is the object of the invention to produce pure nitrous oxide, we prefer to employ phosphorus or arsenic derivatives which are substantially non-volatile under the conditions which obtain in the reaction vessel. As examples of suitable phosphorus compounds we may mention the various ammonium phosphates, such as ammonium dihydrogen ortho phosphate, ammonium meta phosphate, diammonium pyrophosphate, and the like; the various alkali and alkaline earth phosphates, such as trisodium phosphate, disodium acid phosphate, monopotassium acid phosphate, barium pyrophosphate, barium hypophosphate, calcium meta phosphate, calcium hypophosphate, calcium pyrophosphate, magnesium acid ortho phosphate, and related compounds; and in general any of the other phosphorus derivatives such as phosphorous pentoxide, phosphorous trioxide, iron phosphate, phosphomolybdic acid, cobalt phosphate and similar compounds. As examples of suitable arsenic compounds we may mention arsenous oxide, arsenic oxide, arsenic acid, arsenious acid and the acid derivatives such as sodium arsenite, sodium arsenate, potassium arsenate, ammonium arsenite, calcium arsenate and the like. We have also found that compounds derived from molybdenum, silver, and manganese exhibit a desirable effect, although to a lesser degree. As examples of suitable derivatives of these elements we may mention ammonium molybdate, silver nitrate, manganous nitrate and the like.

All these materials produce two effects in the thermal decomposition of ammonium nitrate. In the first place, the materials mentioned catalyze the decomposition to nitrous oxide as evidenced by an increased rate of reaction. In the second place, the materials according to our invention inhibit the side reactions which attend the decomposition of ammonium nitrate to nitrous oxide. As a result, the purity of the gas produced is significantly higher and the evolution of the gas proceeds rapidly and smoothly.

As a specific example of one embodiment of our improved process, we may operate as follows: 600 pounds of ammonium nitrate is introduced into a suitably heated metal retort, adapted for the production of nitrous oxide gas, together with 0.06 pound of ammonium dihydrogen phosphate. The retort is heated until the contents reach the decomposition temperature, when the external heating is discontinued. The reaction is allowed to proceed with evolution and subsequent collection of nitrous oxide until only about 200 pounds of ammonium nitrate remains in the retort, when the reaction is stopped. 400 pounds of fresh ammonium nitrate and 0.04 pound of ammonium dihydrogen phosphate is then introduced into the retort and the mixture is heated again to decomposition temperature, with further production of nitrous oxide. Only after a large number of runs will it be necessary to discard the residual heel of accumulated impurities.

In carrying out our invention, we preferably utilize ammonium nitrate of low content of our catalyst. In the case of soluble phosphates, for example, we find it desirable to have such material present in an amount greater than 0.001% by weight of ammonium nitrate present. Preferably we employ not more than 2% of the catalyst, for example between 0.01% and 0.1% by weight of the ammonium nitrate. The use of relatively higher percentages of the phosphate will be undesirable for economic reasons and beyond a certain point, for example 2%, will bring no further advantage. It will be understood, of course, that with the successive decomposition of ammonium nitrate charges and the addition of fresh phosphate-containing nitrate to the residual undecomposed salt, the content of this or other beneficial added material will build up progressively. Such increased contents, however, are not deleterious to the successful operation of the process. There is furthermore no tendency for the catalyst to react to form gaseous products and pass over with the nitrous oxide.

The advantages of our catalyst may be readily appreciated from laboratory tests and to an even greater degree from actual plant operations. Its use assures greater safety in operation, increased yields and a nitrous oxide of higher purity.

While for purposes of illustration a batch process has been described, it will be understood that our improved method is equally applicable to other modes of operation. Thus for example, we may employ the process described and claimed in our copending application, Serial No. 87,201 filed June 25, 1936. According to this method, the decomposition of ammonium nitrate is carried out in such a manner that a substantially constant ratio is maintained between the amount of ammonium nitrate being decomposed and the amount of catalyst present in the reaction mixture. Thus we may introduce into the retort 60 pounds of ammonium dihydrogen phosphate, for example, and 540 pounds of ammonium nitrate. The contents are brought to the temperature of decomposition of the ammonium nitrate, and the evolved nitrous oxide is collected. Ammonium nitrate in either solid or molten form, or as an aqueous solution, with or without added catalyst, is added to the retort in such a manner that a substantially constant quantity of ammonium nitrate is present in the retort at all times. The particular advantages in this procedure arise from the fact that a substantially constant ratio is maintained between the amount of catalyst and the amount of ammonium nitrate present in the retort, with the result that the course of the reaction is smoother, and N_2O of higher purity is produced. Since the catalyst is substantially

non-volatile under these conditions, there will be no loss of ammonium phosphate. This method of operation is disclosed and claimed in our copending application, Serial No. 87,201 filed June 25, 1936.

It should be apparent also that our improved process and our ammonium nitrate adapted for the efficient production of nitrous oxide make no claims as to temperature limits during the decomposition period but simply require heating to the temperature where the decomposition of the ammonium nitrate produces the desired gas generating rate. Similarly other steps of our process will be the same as those of the prior art. Thus, for example, we may employ our improved catalysts not only with ammonium nitrate added to the retort as such, but also with a mixture of salts such as sodium nitrate and ammonium sulfate, which result in the formation of ammonium nitrate in situ. In fact, many variations in details and conditions of operation may be made, without departing from the scope of the invention. We intend therefore to be limited only by the following patent claims:

We claim:

1. The process of producing nitrous oxide by heating ammonium nitrate to its decomposition temperature, which process comprises maintaining in contact with said ammonium nitrate during the decomposition period a catalyst comprising a compound containing an element selected from the group consisting of phosphorus and arsenic.

2. The process of producing nitrous oxide by heating ammonium nitrate to its decomposition temperature, which process comprises contacting said ammonium nitrate during the decomposition period with an inorganic compound containing a phosphoric acid radical.

3. The process of claim 2, in which said inorganic compound is water-soluble.

4. The process of claim 2, in which said inorganic compound comprises ortho-phosphoric acid.

5. The process of claim 2, in which said inorganic compound comprises ammonium dihydrogen phosphate.

6. The process of claim 2, in which said inorganic compound comprises normal sodium phosphate.

7. The process of claim 2, in which the compound containing a phosphoric acid radical is present in an amount in excess of 0.001% of the weight of ammonium nitrate.

8. A new composition of matter adapted for the production of nitrous oxide by thermal decomposition, said composition consisting essentially of ammonium nitrate and not over 2% of an inorganic compound containing an element taken from the group consisting of phosphorus and arsenic.

9. A new composition of matter adapted for the production of nitrous oxide by thermal decomposition, said composition consisting essentially of ammonium nitrate and not over 2% of an inorganic compound containing a phosphoric acid radical.

10. The composition of claim 9, in which said inorganic compound comprises ammonium dihydrogen phosphate.

11. The composition of claim 9, in which said inorganic compound comprises ortho-phosphoric acid.

12. The composition of claim 9, in which said inorganic compound comprises normal sodium phosphate.

13. The composition of claim 9, in which said inorganic compound is present in an amount between 0.001 and 2% by weight of the ammonium nitrate.

14. The process of producing nitrous oxide by heating ammonium nitrate to its decomposition temperature, which process comprises maintaining in contact with said ammonium nitrate during the decomposition period not over 2% of a catalyst comprising a compound containing an element selected from the group consisting of phosphorus and arsenic.

15. The process of producing nitrous oxide by heating ammonium nitrate to its decomposition temperature, which process comprises maintaining in contact with said ammonium nitrate during the decomposition period a catalyst comprising a compound containing phosphorus.

16. The process of producing nitrous oxide by heating ammonium nitrate to its decomposition temperature, which process comprises maintaining in contact with said ammonium nitrate during the decomposition period not over 2% of a catalyst comprising a compound containing phosphorus.

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