This invention which is a continuation-in-part of application No. 478,552, filed on March 9th, 1943, now United States Patent No. 2,406,172, issued August 20, 1946, relates to processes for oxidising ammonia to oxides of nitrogen by passing a mixture of ammonia and oxygen-containing gas into contact with a catalyst at an elevated temperature, in which the catalyst is formed by an alloy containing platinum and rhodium.

An alloy has already been proposed for the same purpose, namely an alloy of platinum and rhodium containing at least 2% by weight of rhodium, preferably between 5 and 50% especially from 5-25%, the optimum figure being about 10% rhodium and the balance of the alloy being platinum. The alloy is commonly used for the purpose in question in the form of gauze.

For the catalytic oxidation of ammonia by means of such a platinum/rhodium alloy, in order to obtain maximum catalytic efficiency the alloy is made of metals as nearly chemically pure as possible. Any alloy of chemically pure metals has a relatively low tensile strength. The weaving is done upon looms of more or less standard type, similar in design to those used in the textile weaving trade. In view of the fact that the wires from which this particular catalyst gauze is made are commonly of very fine diameter, namely, a few thousandths of an inch, the very greatest care has to be taken in operating these looms to prevent wire breakage which means that only a very low rate of production can be obtained.

The object of the present invention is to provide improved catalysts containing platinum and rhodium, and for the above purpose, free of the disadvantages indicated in the preceding paragraph, that is to say, not only with reference to the difficulty of breakage but also with reference to the limitation of range of alloy constituents. This I find can be done by employment of a platinum/rhodium alloy with which is incorporated a refractory oxide, the material being in the form of a compacted and sintered agglomerate, and the constituents being initially in a finely divided condition.

It is here recorded that for purposes of the present invention whilst the oxide constituent may lie within wide or general limits as in the main application 478,552, now United States Patent No. 2,406,172, issued August 20, 1946, referred to above, the preferred range is more extensive than that specifically mentioned in the above specification and is from 0.01% to 10%. Any suitable oxides may be employed. If hydrogen or other reducing gas be used in the process the oxide should not be easily reducible at the sintering temperature, but if an inert gas be employed this limitation is not required and any refractory oxides may be used. Although I have mentioned 10% as the upper limit for the oxide, all ranges have not necessarily the same merit. In certain circumstances the preferences are respectively up to 1%, up to 2%, up to 5% and, as stated, up to 10%. Whatever amount be used the oxide should be stable with reference to the present process, that is to say, it should be not decomposed during the production process, for example, as explained, not reduced in the presence of hydrogen when hydrogen is employed in the process.

Regarding the constitution of the alloy, it should mainly consist of platinum and rhodium. Although platinum is preferred as the main constituent of the alloy, this is not necessarily so, and the main constituent of the alloy may be rhodium. Ordinarily speaking, the alloy should mainly consist of platinum and should have a rhodium content of from about 1% to 50%, for instance from 2% to 25%, preferably 5% to 10%, the optimum figure being about 10% rhodium with the balance of the alloy being platinum. Similarly for the oxide the permissible percentage may be regarded as not limited. The compacted and sintered agglomerate is sufficiently strong to enable it to be swaged, rolled, drawn or otherwise treated to bring it to the form of a wire, sheet or any other desired conditions.

The present invention consists in an improved process of oxidising ammonia to oxides of nitrogen by passing a mixture of ammonia and oxygen-containing gas into contact with a catalyst at an elevated temperature, the catalyst being formed of an alloy of platinum and rhodium in which the catalyst is prepared from a compacted and sintered agglomerate of the alloy with which is incorporated a suitable oxide.

The invention also consists in a process in accordance with the preceding paragraph in which the alloy consists of platinum.

The invention also consists in a process in accordance with the next but one preceding paragraph in which the alloy consists of rhodium.

The invention also consists in a process in accordance with either of the preceding two paragraphs in which the secondary constituent of the alloy, namely rhodium or platinum as the case may be, comes within one or other of the following ranges, namely, up to 2%, up to 5% and up to 10%.
The invention also consists in a process in accordance with any of the preceding four paragraphs in which the oxide content comprises one or more of the following oxides, which may be obtained by reference to the Periodic Table of Deming, "General Chemistry," fourth edition, said oxides being, namely, (a) thorium oxide; (b) one or more oxides of the alkaline earth metals of group II of the periodic table, namely, calcium, strontium, magnesium, and beryllium; (c) one or more of the oxides zirconia, hafnia, ceric oxide (CeO\textsubscript{2}), and titanium oxide (TiO\textsubscript{2}); (d) aluminum oxide; (e) one or more of the oxides of the rare earth metals which if they are employed in the presence of hydrogen or other reducing gas are not easily reducible at the sintering temperature with the exception of ceria, which is referred to above, the rare earth elements being those with atomic numbers 57 to 62 constituting sub-group 1, 63 to 65 constituting sub-group 2, 66 to 71 constituting sub-group 3, and scandium and yttrium, especially oxides of the elements lanthanum and neodymium; (f) one or more of the oxides of certain members of the fifth group of the periodic table which if they are employed in the presence of hydrogen or other reducing gas are not easily reducible at the sintering temperature, namely, vanadium, columbium and tantalum; and (g) a particular oxide of a member of group VI of the periodic table, namely, the sesquioxide of the metal chromium, that is, chromic oxide (Cr\textsubscript{2}O\textsubscript{3}), any of the above oxides being used alone or in combination among themselves or with one or more other oxides which if they are employed in the presence of hydrogen or other reducing gas are not easily reducible at the sintering temperature, and all the constituents, namely, both metallic and oxide being initially in a finely divided condition; this compacted and sintered agglomerate being swaged, rolled, drawn or otherwise treated to bring it to the form of a wire or sheet or any other desired condition where it may be used as a catalyst as such or as a developed product such as wire gauge.

The invention also consists in a process in accordance with any of the preceding five paragraphs in which the proportion of oxide is from 0.01% upwards but less than 1%, preferably 0.1% to 0.5% of the weight of the metal.

Insofar as the oxidation of ammonia is concerned, the general conditions thereof, other than the specific catalyst here involved as used therein, are like those usually employed in which connection reference is made to United States Patent No. 1,706,655 of C. W. Davis. The process is customarily carried out at atmospheric pressure or higher, e.g., up to 7 atmospheres and more, at a temperature between about 650°C and about 1000°C, the ammonia air mixture containing usually about from nine percent (9%) to eleven percent (11%) ammonia, and sometimes enriched with oxygen, being passed over the catalyst.

The following examples illustrate by way of exemplification only how the preparation of the catalyst may be effected:

**Example 1**

This example used metallic platinum and metallic rhodium. I take 90 grams of finely divided platinum powder, prepared by any suitable method, and 10 grams of rhodium powder. These powders are intimately mixed by well shaking in a suitable container or by any other method which will produce the desired intimate mixture as for instance a "Cyclone" box in which the mixing is accomplished by means of a jet of air. In the mixing process it is desirable to avoid burnishing the particles. The intimate mixture is wetted with 20 cc. of an aqueous solution of thorium nitrate containing the equivalent of 0.25 gram of thorium oxide (ThO\textsubscript{2}). The resultant paste is evaporated to dryness with constant stirring to ensure uniform distribution of the constituents. The resultant powder is then heated to about 850°C in a current of hydrogen to decompose the thorium nitrate to the oxide and to reduce any rhodium oxide which may be present. The resultant powder consists of an intimate mixture of metallic platinum and rhodium together with thorium oxide. This product is sieved, packed into a steel mould and compressed under a pressure of about 30 tons per square inch in order to form a coherent mass. The compressed material is then heated at about 1400°C to 1550°C in hydrogen for about one hour, the effect of this heating being to alloy the rhodium with the platinum, and to sinter the mass into a dense body, sufficiently strong to enable it to be swaged, rolled, drawn or otherwise treated to bring it to the form of a wire sheet or any other desired condition.

**Example 2**

This example uses ammonium chloroplatinate and metallic rhodium.

I take 100 ccs. of distilled water in which is suspended ammonium chloroplatinate in sufficient quantity to yield 0.25 gram of platinum in subsequent decomposition. To this I added 10 grams of rhodium powder and 10 ccs. of an aqueous solution of thorium nitrate containing the equivalent of 0.25 gram of thorium oxide. The whole is then made up to approximately 200 ccs. by the addition of distilled water. The resultant paste is evaporated to dryness with constant stirring to ensure uniform distribution of the constituents. The dried mass is then heated slowly through the range 310°-350°C to decompose ammonium chloroplatinate with the elimination of ammonium chloride and hydrochloric acid and the consequent formation of platinum powder. The temperature is then raised to about 600°C for the decomposition of thorium nitrate to the oxide. The powder is then heated to about 850°C in a stream of hydrogen to reduce any rhodium oxide which may be present. The resultant powder consists of an intimate mixture of metallic platinum and rhodium together with thorium oxide. This product is sieved, packed into a steel mould and compressed under a pressure of about 30 tons per square inch in order to form a coherent mass. The compressed material is then heated at about 1400°C to 1550°C in hydrogen for about one hour, the effect of this heating being to alloy the rhodium with the platinum, and to sinter the mass into a dense body, sufficiently strong to enable it to be swaged, rolled, drawn or otherwise treated to bring it to the form of a wire sheet or any other desired condition.

**Example 3**

This example uses metallic platinum and ammonium hexachlorododate.

I take 90 grams of finely divided platinum, and to this is added an aqueous solution of ammonium hexachlorododate in sufficient amount to yield 10 grams of rhodium on subsequent decomposition, and an aqueous solution of thorium nitrate containing the equivalent of 0.25 gram of thorium oxide (ThO\textsubscript{2}) in sufficient water to form a paste.
with the platinum and rhodium ingredients. This paste is treated in the same way as the resultant paste of Example 2.

**Example 4**

This example uses ammonium chloroplatinate and ammonium hexachlororhodate.

I take 100 ccs. of distilled water in which is suspended ammonium chloroplatinate in sufficient amount to yield 10 grams of platinum on subsequent decomposition. To this is added 50 ccs. of an aqueous solution of ammonium hexachlororhodate containing sufficient salt to yield 10 grams of rhodium on subsequent decomposition. To this is added 10 ccs. of an aqueous solution of calcium acetate containing the equivalent of 0.5 gram of calcium oxide (CaO). The whole is then made up to approximately 200 ccs. by the addition of distilled water. The resultant paste is evaporated, dried, and the heat treatment of 310° C. to 350° C. as applied in Example 2. The temperature is then raised to 850° C. for the conversion of the calcium acetate to calcium oxide. The product is crushed, spread on trays, and re-heated to about 850° C., but in a stream of hydrogen, and the process then proceeds as in Example 2, from the 850° C. stage treatment.

**Example 5**

This example uses ammonium chloroplatinate and rhodium chloride.

I take an aqueous suspension of ammonium chloroplatinate in sufficient amount to yield 90 grams of platinum on subsequent decomposition, and to this is added an aqueous solution of rhodium chloride containing the equivalent of 10 grams of rhodium, and an aqueous solution of calcium acetate containing the equivalent of 0.20 gram of calcium oxide (CaO) in sufficient water to make a paste with the other ingredients. The resultant paste is treated similarly to the resultant paste of Example 4.

**Example 6**

This example employs an alloy of platinum and rhodium.

An alloy of platinum and rhodium, containing 10% rhodium by weight, which has been produced in the usual way is dissolved in aqua regia. Hydrochloric acid is added to the resulting solution which is then concentrated by evaporation. The concentrated solution is then diluted with water followed by hydrochloric acid and again evaporated to decompose nitrate and nitrite compounds. The processes of concentration and dilution are repeated as often as necessary to decompose all nitrate and nitrite compounds. The resultant solution which consists of the chlorides of platinum and rhodium is evaporated to remove as much free hydrochloric acid as possible. A slight excess of a saturated solution of ammonium chloride is added to produce the ammonium chloride complexes of the two metals. Any free hydrochloric acid present is then neutralised by the addition of ammonia thus producing a solution of ammonium hexachlororhodate and ammonium chloride with ammonium chloroplatinate in suspension. To this is added 10 ccs. of an aqueous solution of thorium nitrate containing the equivalent of 0.25 gram of thorium oxide. The whole is then slowly evaporated to dryness with careful stirring. The dried mass is then heated in the same way as the dried mass in Example 2.

This method has the great advantage that rhodium chloride can be relatively easily obtained whereas it is a long and tedious process to dissolve rhodium alone.

**Example 7**

This example using platinum and rhodium chlorides is recommended if a very fine powder is desired.

A solution of platinum and rhodium chlorides, containing the equivalent of 90 grams of platinum and 10 grams of rhodium is made slightly alkaline with caustic soda; sodium formate and formic acid are then added in sufficient quantities to cause, when the solution is boiled, reduction and precipitation of platinum and rhodium. In the place of sodium formate and formic acid any other suitable reducing agents can be used, such as sodium acetate and sodium formate or formaldehyde or hydrazine hydrochloride. Alternatively, the metals can be reduced from solution by use of a metal such as zinc, magnesium or aluminum together with hydrochloric acid, thus producing nascent hydrogen with the subsequent reduction of the platinum and rhodium. The precipitated metals are filtered off and thoroughly washed with a boiling 2% solution of ammonium chloride. The sludge is then mixed with 20 ccs. of a solution of thorium nitrate containing the equivalent of 0.25 gram of thorium oxide. The resultant paste is treated in the same way as the resultant paste in Example 1.

**General**

It is recorded that the invention is not limited by the examples but is as broad as indicated in the statement of invention above.

The required finely divided condition of the metallic starting materials is obtained by any known and suitable process such as precipitation, or decomposition and reduction in hydrogen. Alternatively, they may be prepared by reduction from solutions of the chlorides or any other suitable salt by means of electrolysis. This method can be used for either metal singly or both metals can be co-deposited. The conditions are regulated in such a manner as to ensure that the metals are deposited in the form of a non-coherent fine powder.

In the above examples the oxide constituent may be replaced by an equivalent amount of any of the other oxides stated above. Good alternatives to calcium, for instance, are aluminum or beryllium.

Usually the quantity of the oxide constituent required is from 0.01% upwards but less than 1% of the weight of the metal and preferably about 0.15% to 0.5%.

In the examples the oxide has been introduced by way of the acetate or nitrate but in place thereof any soluble or insoluble salt of the desired metal can be used which can conveniently be introduced into the mixture of metallic powders or salts and which will decompose to the oxide upon heating. For example, thorium oxalate may be used.

In all cases the oxide must be introduced in such a way that it is uniformly and finely dispersed throughout the mass. I find the most satisfactory method is to employ a solution of the equivalent appropriate salt, and after incorporating this with the other ingredients and drying the product, to decompose the salt to the oxide by heat.

As regards the pressures to which the ingredients are subjected, these may vary over a wide
range, as for example from 5-50 tons per square inch, the most appropriate pressure being dependent on the metal or alloy and the fineness of the powder, regard being had to the effect on workability.

The compacted and sintered agglomerate of platinum, rhodium and the oxide constituent is brought into the desired form, say, into the form of a wire and this wire or other form may be developed for the aforesaid ammonia oxidation process, for instance, drawing it into the form of wire gauze or making it into any other suitable form.

It is well known that platinum/rhodium alloys produced by the "normal method" in the wrought or worked condition can be readily re-crystallised to give an equi-axed crystal structure by heating at or above a minimum critical temperature. This recrystallisation takes place more rapidly by heating above the critical temperature.

It is also well known that prolonged heating at or above the critical temperature causes marked crystal growth as a result of the smooth or sharp merging of the small crystals initially formed. This crystal growth causes the metal to become mechanically weak and liable to fracture. Furthermore, under the operating conditions of the ammonia oxidation process herein described, the metal when in the coarse crystalline condition resulting from prolonged heating, is very liable to surface erosion.

I have found that platinum/rhodium alloys, prepared by the methods described in this invention though of a very high degree of chemical purity, have a greatly increased tensile strength and hardness in comparison with wires made without an oxide addition. Consequently there is less wire breakage in the loom, and thereby production can be obtained at a higher rate than with wires without the oxide addition. Furthermore, the general characteristics of the metal make it much more satisfactory to use, for example, there is less tendency for the wire to break in the heddles and the reed of the loom, which is usually the cause of breakage. Briefly, a better type of gauze can be produced by using wire made according to this invention, and that gauze can be made more quickly than the earlier type of gauze.

Further, platinum/rhodium alloy gauzes prepared as described above do not behave in a manner similar to normally produced platinum/rhodium alloys when subjected to heat. The addition of the non-metallic constituent has the effect of preventing normal re-crystallisation. For example, a normally produced platinum/rhodium alloy containing 10% rhodium in the wrought or fibrous condition can be re-crystallised to give an equi-axed crystal structure by heating for 30 minutes at 1000°C, or by heating for a longer period of time in the range 800°C-1000°C. An alloy having the same metallic composition but prepared according to this invention with the non-metallic constituent when heated for the same time to the same temperature reveals on careful micro-examination that the metal has not been re-crystallised to an equi-axed structure. Examination of platinum/rhodium alloys prepared as described above which have been subjected to elevated temperatures even approaching the melting point show that the addition of the non-metallic constituent has prevented normal coalescence and ordered crystal growth.

Careful micrographic examination of the metal after prolonged heating at high temperatures reveals that the attenuated crystalline fibre characteristic of the wrought structure have tended to thicken but the presence of the non-metallic constituent has prevented even in extreme cases normal crystal growth, which may, for instance, cause grain boundaries to develop fully across the diameter of a wire, thus resulting in points of weakness.

At the operating temperature of the ammonia oxidation process herein described, this temperature being but slightly above the critical temperature at which re-crystallisation phenomena in the normal alloy, as a result of which metals produced in ordinary ways undergo marked crystal growth, causing a weakening in such mechanical properties as strength or hardness, the alloy produced according to this invention does not re-crystallise to an equi-axed structure even after prolonged heating but substantially retains the original fibrous structure. Some change in structure may be observed after prolonged heating but this change takes the form of a coarsening of the fibres and is entirely dissimilar from that apparent in an alloy normally produced and subjected to the same heat treatment. The retention of the fibrous structure at the operating temperature of the ammonia oxidation process herein described results in a substantial retention of the initial mechanical properties.

In addition, the resistance to the formation of an equi-axed crystal structure prevents deterioration as a result of crystal erosion which is observed in the alloy produced by the normal method. Any surface deterioration which may be observed in the alloy, made according to this invention, during service is of a superficial nature, and, for example, will not cause diminution in the diameter of a wire to the same extent as that observed in normally produced material. Furthermore, the retention of the fibrous structure and the consequent mechanical properties associated therewith diminishes the possibility of fracture of the wire as a result of the mechanical stresses imposed during the process.

I claim:

1. The process of oxidizing ammonia to oxides of nitrogen, comprising contacting ammonia and oxygen-containing gas at elevated temperature in the presence of a catalyst consisting of an alloy of platinum and rhodium intimately mixed, sintered, and compacted with a relatively small amount of a refractory oxide into agglomerated form.

2. The process of oxidizing ammonia in accordance with claim 1 wherein the rhodium content of the alloy constitutes at least about 1% and does not exceed 25% and wherein the content of refractory oxide constitutes from 0.01% to 10%.

3. The process of oxidizing ammonia in accordance with claim 1 wherein the rhodium content of the alloy constitutes from about 1% to about 10% and the non-metallic constituent constitutes from 0.01% to about 1.9%.

4. The process of oxidizing ammonia to oxides of nitrogen, comprising contacting ammonia and oxygen-containing gas at elevated temperature in the presence of a catalyst consisting of an alloy of platinum and rhodium intimately mixed, sintered, and compacted with a relatively small amount of a beryllium oxide into agglomerated form.

5. The process of oxidizing ammonia to oxides of nitrogen, comprising contacting ammonia and oxygen-containing gas at elevated temperature...
in the presence of a catalyst consisting of an alloy of platinum and rhodium intimately mixed, sintered, and compacted with a relatively small amount of a thorium oxide into agglomerated form.

COLIN JAMES SMITHELLS.

REFERENCES CITED

The following references are of record in the file of this patent: