

UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING ALKALINE-METAL OXID.

No. 798,103.

Specification of Letters Patent.

Patented Aug. 29, 1905.

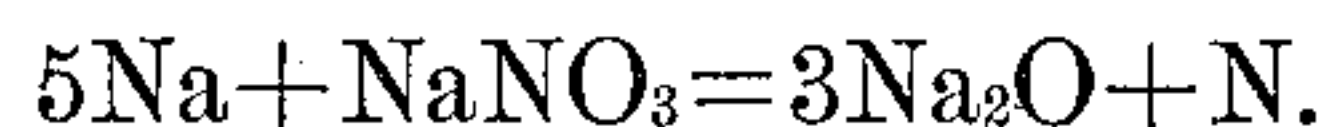
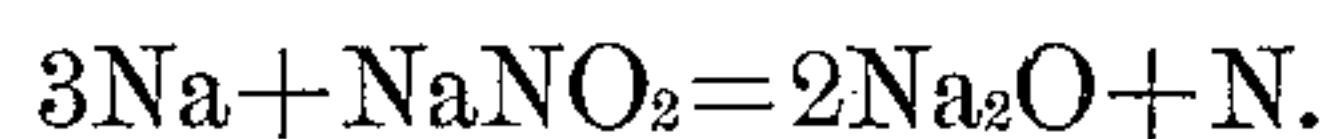
Application filed December 4, 1902. Serial No. 133,891.

To all whom it may concern:

Be it known that I, RUDOLF HUTZLER, doctor of philosophy and chemist, a subject of the King of Bavaria, residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria, Empire of Germany, have invented new and useful Improvements in the Process of Manufacturing Alkali-Metal Oxid, of which the following is a specification.

Neither sodium oxid nor potassium oxid has hitherto been prepared directly from their corresponding nitrate, for the alkali nitrates on heating to a red heat do not yield the oxids, but the superoxids. Further, when alkali nitrate has been heated with the corresponding alkali metal alkali superoxid (Na_2O_2 , K_2O_4) has invariably been formed under the conditions observed.

I have discovered that by taking suitable precautions "alkali nitrates" (under which term I include the nitrates of the alkali-earth metals) can be caused to react with alkali metal in an entirely different manner from that hitherto observed between alkali nitrate and alkali metal—namely, so as to form practically pure alkali oxid, either alone or in admixture with another alkali oxid or alkali-earth oxid, or both. As equivalents of the nitrates in the above process the corresponding nitrites can be employed, in which case the reaction proceeds more quietly, less alkali metal is required, and the apparatus is not attacked so much as when working with the nitrate. When using sodium and sodium nitrate or sodium nitrite, for example, reaction appears to proceed in accordance with the following equations:



From the above equations it is possible to calculate the quantities of the reacting materials required to produce the greatest yield of alkali oxid, and to obtain the best results it is essential to exclude air as far as possible from the reaction. On account of the difficulty of excluding all air from the vessels in which the reaction takes place I generally prefer to employ a slight excess of the alkali metal in order to counteract the effects of such air. When operating so as to produce potassium oxid, it is necessary that the nitrate or nitrite

employed be not in excess of the quantity theoretically necessary to convert the alkali metal into alkali oxid if it is desired to avoid the formation of potassium superoxid, for potassium oxid is oxidized by an excess of nitrate or nitrite to potassium superoxid even at temperatures at which such salt does not give off any free oxygen. Sodium oxid, on the other hand, is not so sensitive to oxidizing agents and is not acted on by excess of nitrate or nitrite, provided either of these latter is not heated beyond its decomposing-point.

The process can be modified in various ways—for example, by heating metallic sodium and potassium nitrate or potassium nitrite or by heating metallic potassium with sodium nitrate or with sodium nitrite or with a nitrate or nitrite of an alkali-earth metal or with mixtures of such bodies, the necessary proportions being calculated in a manner similar to that aforementioned. In all these latter cases of course mixtures of alkali oxid or of alkali oxid and alkali-earth oxid are obtained.

I hereinafter employ the generic term "alkaline-metal oxid" to include not only the monoxid of the alkali metals proper, but also mixtures of the monoxids of the various alkali metals proper, as well as mixtures of the monoxids of one or more alkali metals proper with the monoxid of one or more so-called "alkali-earth metals."

Hereinafter I employ the generic term "nitroxy salt" to include not only the salt of one alkali metal or of one alkali-earth metal with an oxygen acid of nitrogen, but also mixtures of salts of various alkali metals or of various alkali-earth metals with various oxygen acids of nitrogen and mixtures of salts of one and the same alkali metal or alkali-earth metal with various oxygen acids of nitrogen and mixtures of salts of various alkali metals or alkali-earth metals with an oxygen acid of nitrogen and mixtures of salts in which the metallic portion is made up of one or more alkali metals and one or more alkali-earth metals and the acid portion is made up of one or more oxygen acids of nitrogen.

I hereinafter employ the generic term "alkaline metal" to include not only the metals of the alkalies proper, but also the metals of the so-called "alkali earths" proper, as well as mixtures consisting wholly of various

metals of the alkalies proper or wholly of the metals of the alkali earths proper or consisting of mixtures of one or more metals of the alkalies proper and one or more metals of the alkali earths proper.

The following examples will serve to further illustrate the manner of carrying out my invention, the details of which, however, can of course be varied. The parts are by weight, and the temperatures are given in degrees centigrade.

Example 1: Melt about two hundred and fifty parts (250) of metallic sodium in an iron vessel provided with a stirrer and heat the molten metal to a temperature of about two hundred and fifty to three hundred degrees, (250° to 300°.) Then add to it while stirring, gradually and in small portions at a time, one hundred and fifty (150) parts of sodium nitrate previously freed from water, which may be done by melting. The reaction vessel must immediately be closed after each addition, so as to exclude air as much as possible. The reaction is very vigorous and is sometimes accompanied with the appearance of flame. When the entire quantity of sodium nitrate has thus been added, the mass is allowed to cool, and when it is cold a test portion is examined, and if this contains metallic sodium and unchanged nitrate (as may occur in consequence of the addition having been too rapidly effected) the whole must be ground to powder and heated for a short time in a covered crucible to incipient fusion. The product is homogeneous pure sodium oxid.

Example 2: Treat two hundred and fifty (250) parts of metallic sodium in the manner described in Example 1, but with two hundred and twenty (220) parts of sodium nitrite instead of with sodium nitrate. If the resulting product be on examination found not to be homogeneous, it is heated again, as described in Example 1.

Example 3: Melt in an iron vessel provided with a stirring arrangement two hundred and twenty (220) parts of metallic potassium and gradually introduce at a temperature of two hundred and fifty degrees, (250°,) while stirring well, one hundred and fifty (150) parts of potassium nitrite in pieces about as large as peas. While doing this some arrangement should be employed which admits of the nitrite being introduced while excluding air as far as possible from the vessel. The reaction, which at once sets in, is rather violent. The potassium oxid so obtained is when cold a grayish mass, which on being exposed to the air is quickly converted into potassium superoxid. It reacts violently with water, sometimes becoming ignited and oxidizing partly to potassium superoxid. In this example for the potassium nitrite there can be substituted one hundred and seven (107) parts of potassium nitrate; but in this case the walls of the vessel are more strongly attacked in conse-

quence of the more violent reaction. The reaction can be carried out, if desired, by introducing the potassium into the molten nitrite or nitrate.

In place of potassium nitrite or potassium nitrate one hundred and twenty-five (125) parts of sodium nitrite or ninety (90) parts of sodium nitrate can be employed. A mixture of sodium oxid and potassium oxid then results, the potassium oxid preponderating. By reacting with one hundred and thirty (130) parts of sodium on one hundred and fifty (150) parts of potassium nitrite or one hundred and seven (107) parts of potassium nitrate mixtures of sodium oxid and potassium oxid are obtained in which the sodium oxid preponderates. According as one or other of these oxids preponderates, the properties of the mixture more nearly approach the properties of such oxid. Generally speaking, they are more stable against the action of air than pure potassium oxid, but act chemically more energetically than pure sodium oxid.

Example 4: Introduce one hundred and thirty-five (135) parts of calcium nitrite or one hundred (100) parts of calcium nitrate into two hundred and fifty (250) parts of metallic potassium, proceeding as set forth in Example 3. A mixture of potassium oxid and calcium oxid results. The calcium nitrite and nitrate can be replaced by the corresponding quantity of nitrite or nitrate of strontium or barium.

Example 5: Melt in an iron vessel provided with a stirring arrangement two hundred and fifty (250) parts of metallic sodium and then introduce gradually at a temperature of two hundred and fifty degrees, (250°,) while stirring well, two hundred and thirty (230) parts of perfectly anhydrous calcium nitrite or one hundred and seventy (170) parts of perfectly anhydrous calcium nitrate, taking care to exclude air as far as possible. When employing nitrate, the reaction is more violent than when employing nitrite and can be moderated by employing anhydrous caustic alkali as a diluent.

Should the calcium salt have been added too quickly, so that small quantities of unconverted metallic sodium and calcium salt remain in the reaction product, the mass can be finely ground and heated to a sufficient temperature for a short time in a covered vessel, and a homogeneous and pure mixture of sodium oxid and calcium oxid be thus obtained.

In the above example the calcium salt can be replaced by the corresponding quantity of the strontium or barium salt. In this case mixtures of sodium oxid and strontium or barium oxid are obtained.

In all the above examples alloys of sodium and potassium as also mixtures of the various nitroxy salts—that is, nitrites and nitrates—can be employed, and the reactions

can be carried out in the presence of a diluent, such as anhydrous caustic alkali, in which case they are less violent.

I claim—

- 5 1. The process of manufacturing alkaline-metal oxid by heating a nitroxy salt with alkaline metal while excluding air and in the presence of a diluent until alkaline-metal oxid is produced.
- 10 2. The process of manufacturing alkaline-metal oxid by heating a nitroxy salt with alkaline metal while excluding air until alkaline-metal oxid is produced.
- 15 3. The process of manufacturing alkaline-metal oxid by heating a nitroxy salt with alkaline metal until alkaline-metal oxid is produced.
- 20 4. The process of manufacturing alkaline-metal oxid by heating a nitroxy salt with metallic sodium while excluding air and in the presence of a diluent until alkaline-metal oxid is produced.
- 25 5. The process of manufacturing alkaline-metal oxid by heating a nitroxy salt with metallic sodium while excluding air until alkaline-metal oxid is produced.
- 30 6. The process of manufacturing alkaline-metal oxid by heating a nitroxy salt with metallic sodium until alkaline-metal oxid is produced.
7. The process of manufacturing alkali-

metal oxid by heating an alkali-metal nitroxy salt with metallic sodium while excluding air and in the presence of a diluent until alkali-metal oxid is produced. 35

8. The process of manufacturing alkali-metal oxid by heating an alkali-metal nitroxy salt with metallic sodium while excluding air until alkali-metal oxid is produced.

9. The process of manufacturing alkali-metal oxid by heating an alkali-metal nitroxy salt with metallic sodium until alkali-metal oxid is produced. 40

10. The process of manufacturing sodium oxid by heating sodium nitrite with metallic sodium while excluding air and in the presence of a diluent until sodium oxid is produced. 45

11. The process of manufacturing sodium oxid by heating sodium nitrite with metallic sodium while excluding air until sodium oxid is produced. 50

12. The process of manufacturing sodium oxid by heating sodium nitrite with metallic sodium until sodium oxid is produced. 55

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

RUDOLF HUTZLER.

Witnesses:

JOHN L. HEINKE,
JACOB ADRIAN.