UNITED STATES PATENT OFFICE.

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PURIFICATION OF MIXTURES CONTAINING NITRIDS.

1,102,715. Specification of Letters Patent. Patented July 7, 1914.

No Drawing. Application filed June 20, 1910. Serial No. 567,928.

To all whom it may concern:

Be it known that we, CARL BOSCH, Ph. D., and ALWIN MITTASCH, Ph. D., chemists, subjects, respectively, of the King of Prussia and the King of Saxony, residing at Ludwigshafen-on-the-Rhine, Germany, have invented new and useful Improvements in the Purification of Mixtures Containing Nitrids, of which the following is a specification.

Nitrids which have been prepared by means of atmospheric nitrogen from compounds of silicon, aluminium, titanium, zirconium, beryllium, and the allied elements, generally contain impurities, unless absolutely pure materials have been employed in their manufacture. Such impurities include metallic iron, coal, silicates, metallic carbids, silicids, phosphids, sulfids, and the like, and some at least of these are troublesome or even dangerous when the products containing them are stored, or transported, or used, for instance, as artificial manure.

We have now discovered that the nitrids can be purified from these impurities by suitably treating the crude mixtures with an acid or with an oxidizing agent in a suitable manner, and that the impurities can be either removed or rendered harmless, while the nitrids are not attacked or very little attacked.

The quantity and concentration of the acid or oxidizing agent to be used varies according to the nature of the crude nitrid which is to be purified, and depends both on the impurities to be removed and on the nature of the nitrid itself. Thus for instance technical silicon nitrid is attacked only slowly by a considerable excess of acid, whereas aluminium nitrid should not be subjected to the energetic action of acid, although it is relatively stable against the action of dilute acids.

In carrying out our invention, a very great variety of acids or of oxidizing agents can be employed. Either aqueous solutions of acids can be used, or solutions of acid salts, such as bisulfates, or gaseous acids, such as hydrochloric acid, can be employed, and the treatment can be carried out in the cold, although, more generally, especially when there are considerable quantities of impurities to be removed, we prefer to work at a raised temperature. As examples of oxidizing agents which can be used according to our invention, we mention ferric chlorid, bichromates, and the like, which can be employed in the form of solution, if desired, while warming, or the crude mixture can be heated in the dry state with a quantity of manganese dioxid, and the heating can be carried out, if desired, in the presence of a flux such as fluorspar. Another simple and advantageous method of effecting the oxidation is to make use of the oxygen of the air, and for this purpose the crude nitrid can be treated in a damp condition or in suspension with air, preferably at a raised temperature and either in the presence or not of oxygen carriers, such for instance as compounds of copper, cerium, and vanadium; or the dry mixture can be heated while a current of air is passed over it. If the temperature be raised to about 700° C. any coal remaining in the mixture will be burnt, and this is often advantageous. This last mentioned method can be easily carried out in practice in the furnace in which the mixture containing the nitrid has been produced, by passing a moderate current of air through the furnace as soon as the temperature therein has fallen to about 700° C., or lower. Instead of air, other suitable oxidizing agent, such for instance as steam or carbon dioxid can be employed. The action of an acid and an oxidizing agent according to this invention can be combined, for instance, the product can be treated with dilute acid and air then be passed over it, while heating, or the crude product can first be treated with air at a low red heat and subsequently be treated with acid. Silicon-nitrogen compounds can thus be obtained in a very pure condition. The process of our invention can be applied to mixtures of nitrids. The process of our invention is also of particular value, since the products obtained contain a greater percentage of combined nitrogen than do the impure mixtures.

The following examples will serve to illustrate further how this invention can be carried into practical effect, but the invention is not limited to these examples.

Example 1: Stir together at ordinary temperature fifty kilograms of crude aluminium nitrid, one hundred liters of water, and two liters of forty-eight per cent. sulfuric acid. Allow the mixture to stand for

several hours, filter, wash, and dry. The resulting product does not evolve poisonous gases on standing in the air. During the treatment, easily decomposable sulfids, silicids, and phosphids are acted upon by the sulfuric acid, and sulfuretted hydrogen, silicon hydrid and phosphorus hydrid are evolved.

Example 2: Treat for two hours with a current of steam, aluminium-silicon nitrid which has been prepared by heating a mixture of chamotte powder and coal in the presence of a current of nitrogen. The treatment should be carried out in a clay tube at a temperature of from four hundred to six hundred degrees centigrade. The purification can be carried out even more quickly by passing a small quantity of gaseous chlorin over the mixture. The mixture is free from decomposable silicids, carbids, and the like. During the treatment easily decomposable sulfids, silicids, phosphids and carbids are decomposed, giving rise either to hybrids of sulfur, silicon and phosphorus and hydrocarbons or carbon dioxid and sulfates, silicates and phosphates according to the degree to which oxidation is carried on.

Example 3: Digest for some hours, at 50° C., crude zirconium nitrid (prepared from zirconium oxid, carbon, and nitrogen) with a solution of ferric chlorid. The product on being treated with hydrochloric acid no longer gives rise to objectionable vapors. During the treatment, easily decomposable sulfids, silicids, phosphids and carbids are acted upon, some of the sulfur, silicon and phosphorus being evolved in the form of gaseous compounds thereof, while the remainder is converted into sulfates, silicates and phosphates. Carbon dioxid is also evolved.

Example 4: Heat crude silicon nitrid at a temperature of about seven hundred degrees centigrade, in a fairly quick current of air, until the gases leaving the vessel no longer contain any carbon dioxid, then allow the mass to cool, boil it with dilute hydrochloric acid, and wash, and filter it. The relative contents of nitrogen are raised several per cent. in this way. During the treatment with air, the carbon which is left unaltered during the production of the silicon nitrid is oxidized and escapes in the form of carbon dioxid, while the subsequent treatment with acid removes the soluble oxids, carbonates and sulfates.

In manners similar to those described in the foregoing examples other nitrids, such as those of titanium, beryllium, and mixtures thereof with aluminium nitrid and with silicon nitrid, can be purified.

Now what we claim is:—

1. The process of purifying mixtures containing silicon nitrid by oxidizing such mixtures with air at a raised temperature while practically avoiding the formation of ammonia substantially as hereinbefore described.

2. The process of purifying mixtures containing silicon nitrid by oxidizing such mixtures with air at a raised temperature and then treating the resulting product with dilute sulfuric acid, while practically avoiding the formation of ammonia substantially as hereinbefore described.

In testimony whereof we have hereunto set our hands in the presence of two subscribing witnesses.

CARL BOSCH.
ALWIN MITTASCH.

Witnesses:
J. ALEC. LLOYD,
ERNEST L. IVES.