UNITED STATES PATENT OFFICE.

LEOPOLD FRIEDEBERGER, OF BERLIN, GERMANY, ASSIGNOR TO THE VULKAN, GESELLSCHAFT FÜR SELBSTZÜNDENDE GLÜHKÖRPER MIT BESCHRÄNKTER HAFTUNG, OF SAME PLACE.

PROCESS OF MANUFACTURING IGNITERS FOR GAS.

SPECIFICATION forming part of Letters Patent No. 640,554, dated January 2, 1900.

Application filed September 2, 1899. Serial No. 729,378. (No specimens.)

To all whom it may concern:

Be it known that I, LEOPOLD FRIEDEBERGER, a subject of the King of Prussia, German Emperor, residing at Berlin, in the Kingdom of Prussia, German Empire, have invented a new Process of Manufacturing Igniters for Gas; and I do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to the manufacture of ignition masses or igniters for gas by means of metals of the platinum group, and has for its object to so improve the manufacturing process that long-living and reliable igniters result.

The attempts hitherto made to use the catalytic force exerted by the metals of the platinum group when in an extremely finely-divided state for lighting gas-burners have been restricted to the employment of said metals either in the state of "sponge" or "black" applied in a coherent layer or embedded in the pores of a refractory mineral support. These sponge or black igniters do not, however, constitute a satisfactory solution of the problem, inasmuch as they lose their catalytic capacity after a comparatively short period of exposure to the air. Moreover, the platinum sponge and black have proved to be greatly lacking in resistance to the shocks and frictional contact of the current of gas.

The attempt to obtain igniters of longer life by calcining a mixture, prepared by way of solution, of salts of refractory oxids, such as the oxids of earth metals—for instance, nitrate of thorium—with platinic chlorid—that is to say, hydrogen-platinum chlorid ($H_2PtCl_6+6H_2O$)—has not resulted in a perfect solution of the problem. Such igniters require a body of metallic platinum—for instance, a wire or several wires—to be located within their mass in order to store the heat produced by the action of the sponge or black, so that a certain duration of contact between the igniter and the gas to be ignited is necessary to cause the former to act. Moreover, there is a great liability of the igniting composition separating from the wire or wires and of the cracking of the igniting mass owing to the difference between the expansion and contraction coefficients of the two. Besides, platinum sponge or black prepared from platinic chlorid always retains some undecomposed chlorid, which, being a hygroscopic substance, renders the igniter unreliable in damp weather.

I have discovered that with mixtures of the last-named description a quicker igniting action can be obtained and the life of the igniter considerably lengthened when the "platinic chlorid," by which term is meant hydrogen-platinum chlorid, ($H_2PtCl_6+6H_2O$,) is not used alone in combination with the earth oxid, but is intermixed with a cyanogen compound of platinum. Platinum cyanids—the single cyanid as well as the composite ones—besides aiding in driving out the chlorin, as they are very energetic reducing agents, have the property of yielding on reduction by heat the platinum in the metallic state, and not, as the chlorids do, in the form of sponge or black. Thus when a mixture of platinic chlorid with a platinum cyanid is reduced by the action of heat a sponge results which is intimately intermingled with very fine laminæ of metallic platinum. When brought into contact with illuminating-gas, such mixture shows a very rapid-growing red, and an almost instantaneous lighting of the gas takes place. Thus the use of platinic chlorid intermingled with a platinum cyanid not only improves the lighting action of the resulting igniter, but also simplifies the manufacture, as it allows the embedding of special platinum bodies in its mass to be dispensed with. Moreover, as the metallic particles of platinum are finely distributed throughout the whole mass the liability to crack is greatly reduced. However, the igniters so prepared have proved to retain some undecomposed chlorid, which by its absorption of moisture renders the ignition unreliable in damp weather. By further experiments it has been discovered that this hygroscopicity of the igniter is entirely removed by the addition of a "refractory acid," by which I mean the oxid of a non-metallic or acid-forming element which is heat-resisting (or a salt leaving behind such acid on calcining) to the mixture,

such addition having the effect of expelling the last trace of chlorin. By properly applying the discoveries stated an igniter is obtained which will not only ignite the gas with certainty in any state of the weather, but which maintains its igniting capacity for a very long time. This result is obtainable with any metal of the platinum group or any mixture of such metals.

The essence of the present invention accordingly consists in manufacturing gas-igniters by calcining an intimate mixture of a salt yielding a refractory oxid, a chlorid of a metal of the platinum group, a cyanid of a metal of the platinum group, and a chlorin-expelling agent—that is to say, a refractory acid or a salt leaving behind such acid. Both the cyanids and the chlorids may be used either in the form of uncompounded or compounded salts. Examples of the latter are, for instance: (*a*) Cyanid of barium and platinum, ($BaPtCy_4+4H_2O$;) cyanid of magnesium and platinum, ($MgPtCy_4+7H_2O$;) cyanid of ammonium and platinum, $(NH_4)_2PtCy_4+2H_2O$; cyanid of zinc, platinum, and ammonium, ($ZnPtCy_4+2NH_3+H_2O$;) cyanid of thorium and platinum, ($ThPt_2Cy_8+16H_2O$,) and the like or corresponding cyanids of the other metals of the platinum group. (*b*) Chlorid of thorium and platinum, ($PtCl_4+ThCl_4+12H_2O$;) chlorid of magnesium and platinum, chlorid of ammonium and platinum, ($PtCl_4+2NH_4Cl$,) and the like or corresponding chlorids of the other metals of the platinum group.

As refractory oxids all oxids of the alkaline-earth metals and the earth metals may be used in the form of such salts as are decomposable by heat—as, for instance, nitrate of thorium, nitrate of magnesium, nitrate of zinc, and the like.

As chlorin-expelling agents may be used: silicic and fluorhydric acid, fluosilicic acid, boric acid, phosphoric acid, and the like, either as such or in the form of decomposable compounds, such as alkaline silicates, chlorid of silicon, organic silicon compounds, soluble borates, soluble phosphates, and the like.

I prefer to use as most advantageous platinic chlorid or hydrogen-platinum chlorid, ($H_2PtCl_6+6H_2O$,) together with the double cyanid of barium and platinum, ($BaPtCy_4+4H_2O$,) as the metal-yielding component and nitrate of thorium as the refractory oxid-yielding component, in combination with silicic acid as the chlorin-expelling component. The employment of silicic acid has, in addition to its very energetic expelling action on the chlorin, the important technical advantage that it enables, by means of the impregnation method usual in the manufacture of incandescent mantles, shaped igniters to be manufactured in which a large surface is combined with great resisting power to shocks and permanence of shape.

In carrying out the invention in its most perfect form known to me I proceed as follows: A fabric of cotton (wool, silk, asbestos, or the like) is first impregnated with a solution of water-glass, (soluble silicate of potassium or sodium,) and after cautious drying it is treated with a mineral acid, preferably hydrochloric acid, whereby the alkaline silicate is decomposed and its silicic acid caused to remain behind in the gelatinous state. The thus-silicified fabric is impregnated with a watery solution containing twenty-five parts hydrogen-platinum chlorid, platinic chlorid, ($H_2PtCl_6+6H_2O$,) six parts double cyanid of barium and platinum, ($BaPtCy_4+4H_2O$,) and nineteen parts of nitrate of thorium in fifty parts water. After drying the impregnated silicified fabric is cut into pieces of desired size and form, and then these pieces are exposed to the action of heat, so as to reduce the thorium nitrate to thoria and the platinum salts to platinum. Thus a withstanding refractory structure is obtained intermingled with extremely fine particles of platinum.

The proportions for the mixture given in the above example are those which I prefer to use, but may be varied within wide limits.

If it is desired to use the invention for manufacturing the igniting composition in the condition of a formless mass, this may be obtained by mixing the aqueous solution of thorium nitrate and said platinum salts with pure hydrated silicic acid, evaporating the mixture to dryness on the water-bath and calcining the residue, whereby a crumbly mass is obtained. In like manner as above I proceed with the other component substances cited as equivalents.

Having fully described my invention, what I desire to claim, and secure by Letters Patent, is—

1. The process of manufacturing igniters for gas which consists in preparing a mixture of a salt of an earth metal, a chlorid of a metal of the platinum group, a cyanid of a metal of the platinum group, and a chlorin-expelling agent, and calcining, substantially as and for the purpose stated.

2. The process of manufacturing igniters for gas which consists in preparing a mixture of thorium nitrate, platinic chlorid, double cyanid of barium and platinum, and silicic acid, and calcining, substantially as and for the purpose stated.

3. The process of manufacturing igniters for gas which consists in impregnating a fabric with water-glass, treating the impregnated fabric with a mineral acid, impregnating anew with a solution containing thorium nitrate, platinic chlorid and double cyanid of barium and platinum, drying and calcining, substantially as and for the purpose stated.

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

LEOPOLD FRIEDEBERGER.

Witnesses:
L. PINK,
C. SULNO.