

# UNITED STATES PATENT OFFICE.

EMIL GÜNTHER AND RUDOLF FRANKE, OF EISLEBEN, GERMANY.

## PROCESS OF TREATING METALLIC ORES OR MATTES.

No. 879,633.

Specification of Letters Patent.

Patented Feb. 18, 1908.

Application filed June 18, 1907. Serial No. 379,535.

To all whom it may concern:

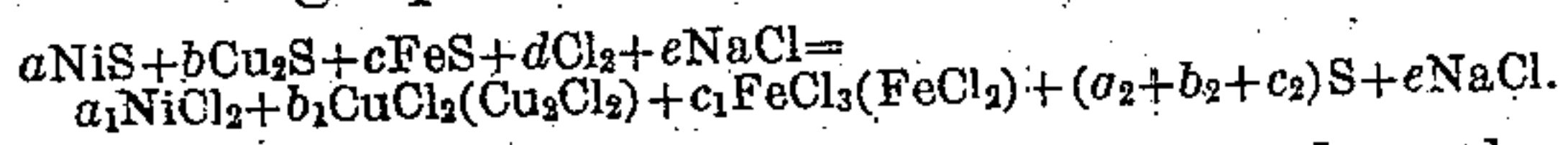
Be it known that we, EMIL GÜNTHER and RUDOLF FRANKE, citizens of the German Empire, and residents of Eisleben, Germany, have invented an Improved Process of Treating Metallic Ores or Mattes, of which the following is a full, clear, and complete specification.

The invention is directed more particularly to the treatment of nickel and copper-containing magnetic pyrites and the separating of nickel and of copper contained in such ores. It is known that the metals contained in the said ores can be concentrated by converting the ores into matte or copper-nickel-regulus which may be done by treating the ores in suitable furnaces. However till now there exists no satisfactory process for obtaining the metals themselves from said copper-nickel-regulus.

The object of this invention now consists in a process of treating the said copper-nickel-regulus and of separating the metals from same in an economical manner.

Our new invention consists broadly in bringing the copper-nickel-regulus to reaction with chlorin either in the form of gas or *in statu nascendi* with the effect that chlorids of copper and nickel are formed and in processes of separating the pure metals from said combinations with chlorin.

The steps for carrying our invention into practical operation are different depending from the form in which the chlorin is brought to reaction with the copper-nickel-regulus. If the chlorin is used in the form of gas we prefer to proceed as follows: The ground regulus is introduced into a closed drum together with the solution of a chlorid, such as sodium chlorid, calcium chlorid, magnesium chlorid, subchlorid of copper and so on and treated with chlorin gas. The reaction which takes place if the temperature is not too much raised may be represented by the following equation:



From this equation it can be seen that the sulfids of the metals are converted into the corresponding chlorids or subchlorids, while at the same time sulfur is set free. Under practical conditions a more or less part of the sulfur contained in the copper-nickel-regu-

lus is not obtained in chemical pure condition, but in the form of sulfuric acid. In order to reduce the quantity of sulfuric acid it is necessary to take care that the temperature is permanently kept at an invariable point.

The metals contained in the copper-nickel-regulus being converted into the form of chlorids, the solid particles are separated from the solution and the solution is freed from sulfuric acid and other impurities so that, technically speaking, a pure nickel-copper-solution is obtained. This nickel-copper-solution is electrolyzed with insoluble anodes. Copper is deposited at the cathode while at the anode chlorin is developed. The chlorin may be used for treating new portions of copper-nickel-regulus. The electrolyte becoming poorer in copper during the electrolyzing process, fresh copper-nickel-solution is added continuously or intermittently till the contents of the bath in nickel is raised to certain desired concentration. Now the bath is freed from copper preferably by electrolysis and by precipitating the last traces of the copper by chemical reagents, for instance by metallic nickel. The bath solution purified from copper and forming then a solution of subchlorid of nickel is likewise electrolyzed after purification with insoluble anodes. In this electrolyzing process chlorin is again set free and may be used for treating fresh portions of the copper-nickel-regulus. The nickel is deposited at the cathode in the same way as in the former electrolyzing process the copper.

The solid mass separated from the solution at the end of the chlorin treatment substantially consists of sulfur and small portions of sulfids. The sulfur may be extracted by suitable solvents whereas the sulfids are added to fresh portions of copper-nickel-regulus and again treated with chlorin.

In a modified method of carrying the invention into practical operation we make additions containing gold, silver or other precious metals to the copper-and nickel-containing ores or to the copper-nickel-regulus. If copper-nickel-regulus into which precious metals have been incorporated in the said way is treated with chlorin gas, as above stated, the precious metals remain in



the solid residue if excess of chlorin is avoided and may easily be obtained therefrom if chlorin in excess is admitted gold may go into solution forming chlorid of gold which is precipitated on later cleaning of the solution.

The process may also be used for producing nickel free from copper from the so-called concentration nickel-regulus with about 75% nickel and about 0.2% copper. In this instance the regulus is digested in the above manner with chlorin, whereupon the nickel-solution is chemically purified and electrolyzed with insoluble anodes.

If it is intended to use the chlorin *in statu nascendi* for treating the copper-nickel-regulus we proceed as follows: The copper-nickel-regulus is used as anode in an electrolyzing process in which the electrolyte is formed of a hydrochloric solution of copper-chlorid in mixture with an alkali- or earthy alkali-chlorid, whereas the cathode is formed of a sheet of copper. In such electrolyzing process at the anode chlorin is produced which converts the sulfids of the metals into the corresponding chlorids liberating at the same time sulfur. The effect of the chlorin *in statu nascendi* therefore is quite analogous to the effect in the previously described process of treating the copper-nickel-regulus with chlorin in the form of gas. The chlorin which is developed by the electrolytic decomposition of the bath solution is entirely used for bringing metal into solution. At the cathode copper is deposited. In view of the fact that at the cathode more copper is deposited than is dissolved at the anode, it is necessary to introduce continuously or intermittently copper salt into the bath which may be produced in the manner hereafter described. In the bath solution nickel accumulates, whereas the contents in copper is kept at an invariable suitable concentration. If after a certain time the concentration of the bath solution in nickel, iron, and other salts is raised to a point that it interferes with the depositing of the copper, the bath solution is drawn off and electrolyzed in other vats with insoluble anodes in order to free it as far as possible from copper and finally the last portions of copper are chemically deposited. In this way a chemical pure nickel-subchlorid-solution is obtained and electrolyzed with insoluble anodes. In this way pure nickel is deposited at the cathode, whereas at the anode chlorin is developed which is just sufficient for treating copper ores containing oxygen or sulfur combinations of copper with the effect of producing the copper salt which is necessary in order to carry out the electrolyzing process of the copper-nickel-regulus after treating with chlorin *in statu nascendi*.

The above process may also be used for

treating concentrated nickel-regulus and for producing nickel free from copper from such regulus.

We are aware that it has already been proposed to treat ores and matte with chlorin. However in this instance the products of reaction were afterwards treated with hydrochloric acid or with other reagents or the metal chlorids were converted into sulfates, whereas in our process the products of conversion which are obtained after treating the copper-nickel-regulus with chlorin are directly used for depositing the metals contained therein. Also the Browne process in which copper-nickel-matte is at first roasted offers disadvantages which are avoided in our process, such disadvantages consisting especially in the difficulty of completely absorbing the roasting gases.

We wish to be understood that in the following claims the term copper-nickel-regulus is intended to cover all kinds of matte containing copper and nickel even if one of these two metals is only present in very small portions. Furthermore the term alkali is used in a broad sense so as to cover not only the alkalies properly spoken but also the so-called earthy alkalies.

Having now described our invention, what we claim and desire to secure by Letters Patent is:

1. In extracting metallic ores and matte the method of producing nickel salt solution for electrolytic deposition of nickel consisting in subjecting copper and nickel containing concentrated regulus to electrolytic action as anode in a bath of chlorid of copper with addition of chlorid of alkali in presence of free hydrochloric acid, introducing copper salt into the bath during the electrolytic process separating the solution when rich in nickel from the solid residue of the anode and eliminating the contents in copper from the solution.

2. The method of obtaining pure metallic copper and nickel from copper and nickel containing regulus consisting in subjecting the copper-nickel-regulus to electrolytic action as anode in a bath containing chlorid of copper with addition of chlorid of alkali in the presence of free hydrochloric acid with the effect of electrodepositing metallic copper at the cathode, introducing chlorid of copper into the bath during the electrolytic process, separating the solution when rich in nickel from the solid residue of the anode, electrolyzing the drawn off solution with insoluble anodes for electrolytically depositing the main portion of copper contained therein, chemically precipitating the rest of the copper out of the bath, electrolyzing the nickel salt solution obtained in this way with insoluble anodes with the effect of electro-

depositing pure metallic nickel, using the  
chlorin formed at the anode for producing  
chlorid of copper from suitable copper ores,  
and using such chlorid of copper as elec-  
5 trolyte when subjecting fresh charges of  
copper-nickel-regulus, as anode, to elec-  
trolytic action.

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

EMIL GÜNTHER.  
RUDOLF FRANKE.

Witnesses:

VILMA FRANKE,  
RUDOLPH FRICKE.