July 3, 1945. R. B. SCHAAL 2,379,659

REFINING OF COBALT ORES

Filed Dec. 24, 1940 6 Sheets-Sheet 1

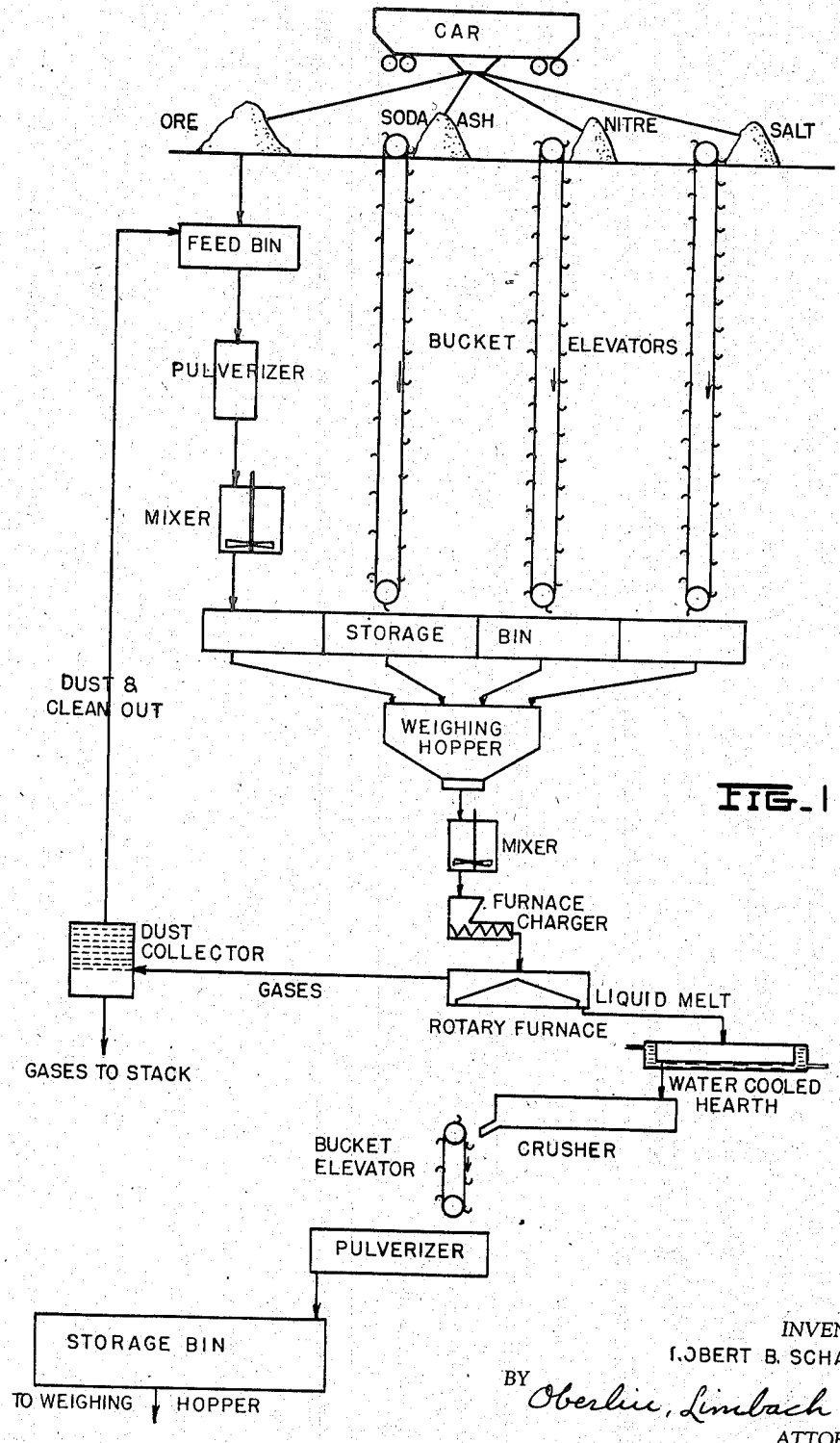

FIG. 1

INVENTOR.
ROBERT B. SCHAAL
BY Oberlin, Limbach & Day
ATTORNEYS.

July 3, 1945. R. B. SCHAAL 2,379,659

REFINING OF COBALT ORES

Filed Dec. 24, 1940 6 Sheets-Sheet 2

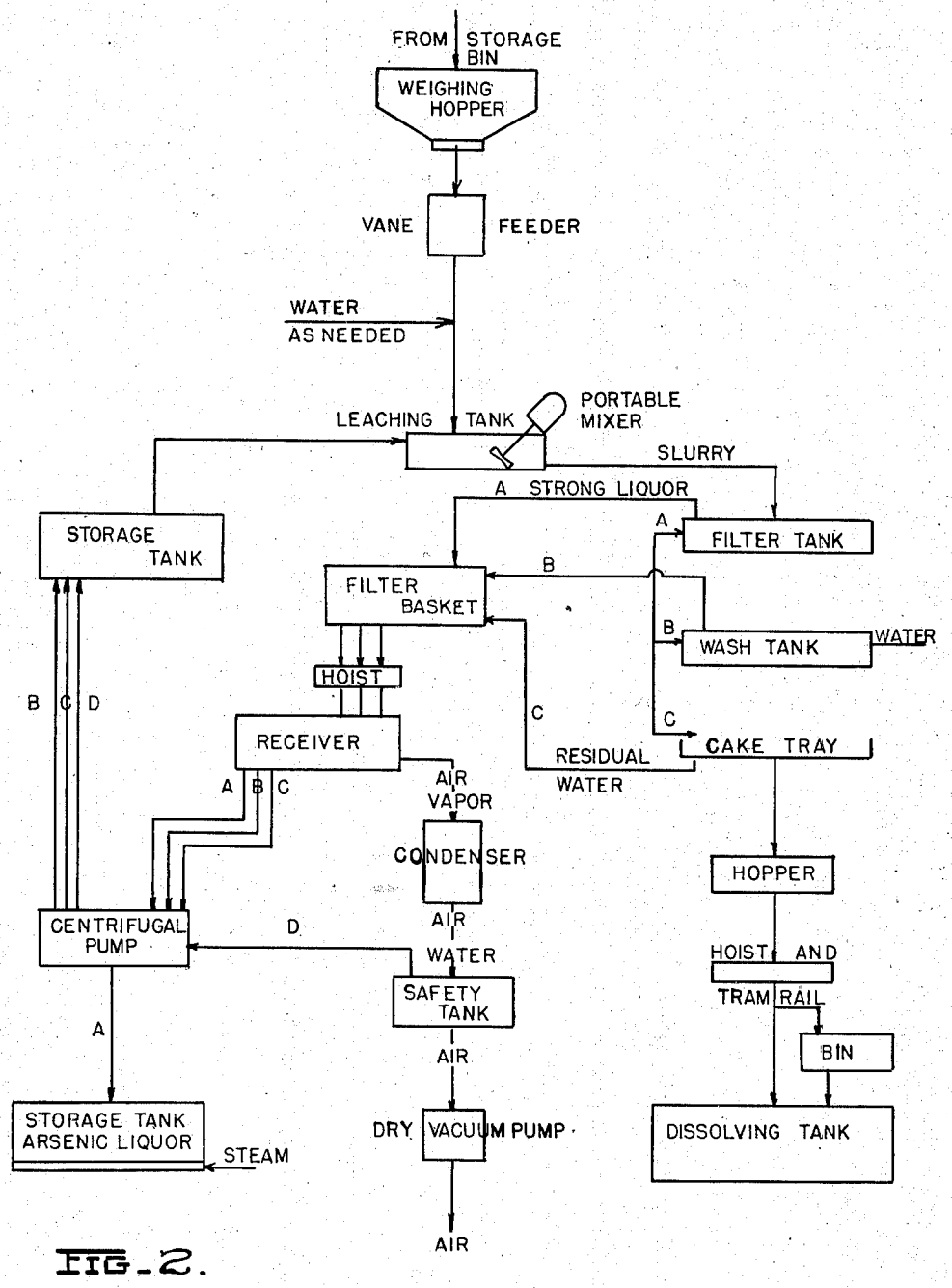

FIG. 2.

INVENTOR.
ROBERT B. SCHAAL

BY Oberlin, Limbach & Day
ATTORNEYS.

July 3, 1945. R. B. SCHAAL 2,379,659

REFINING OF COBALT ORES

Filed Dec. 24, 1940 6 Sheets-Sheet 3

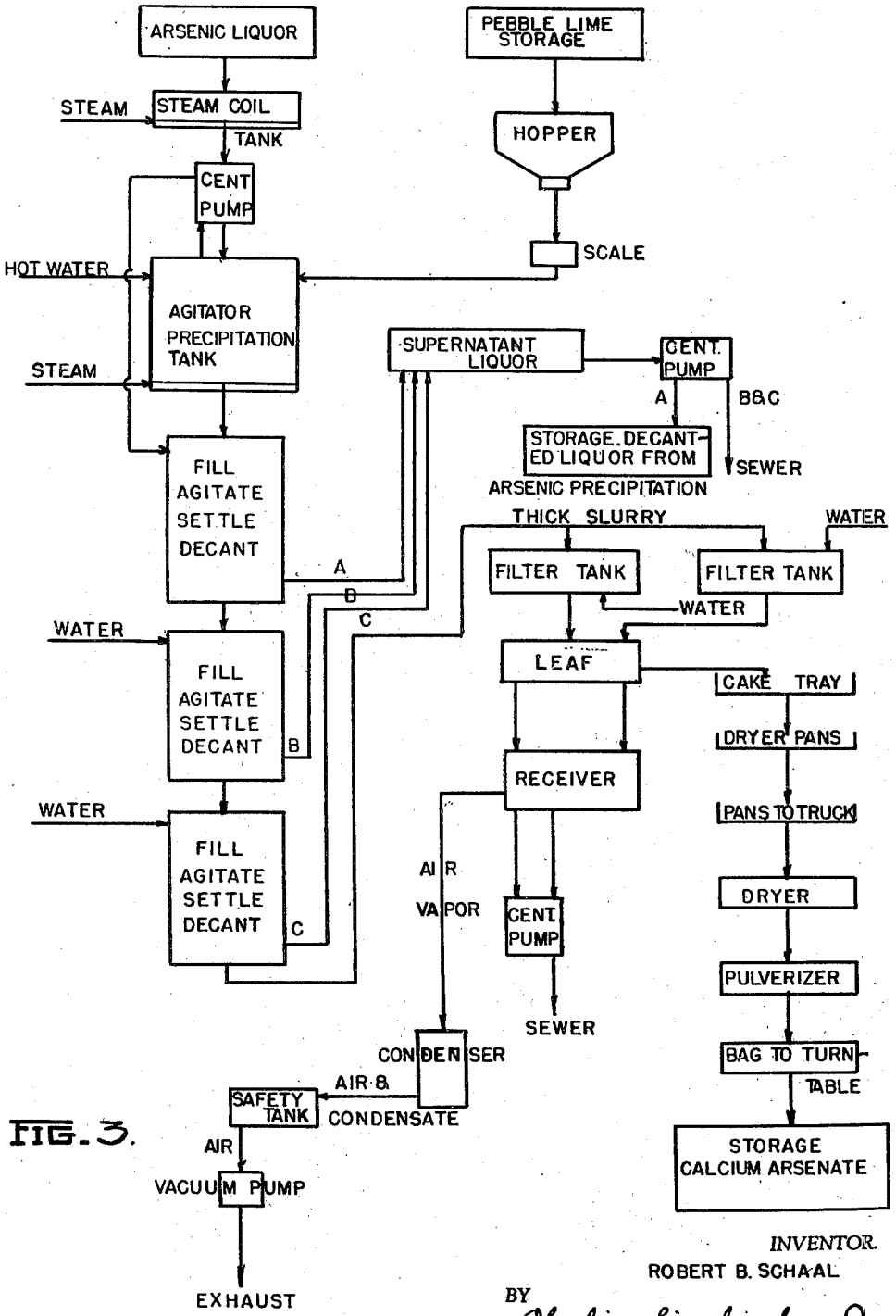

FIG. 3.

INVENTOR.
ROBERT B. SCHAAL
BY Oberlin, Limbach & Day
ATTORNEYS.

July 3, 1945. R. B. SCHAAL 2,379,659

REFINING OF COBALT ORES

Filed Dec. 24, 1940 6 Sheets-Sheet 4

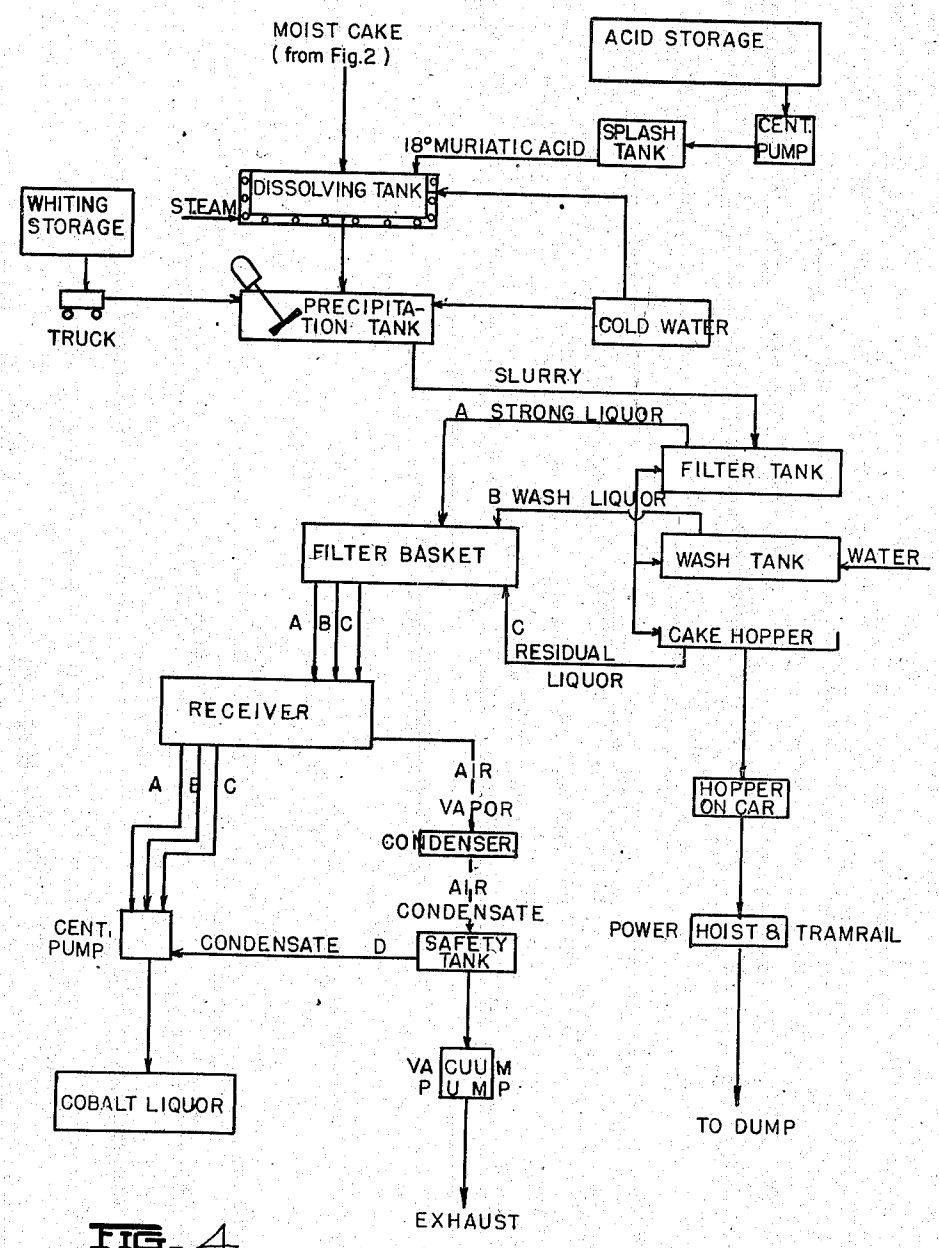

FIG. 4.

INVENTOR.
ROBERT B. SCHAAL.
BY
Oberlin, Limbach & Day
ATTORNEYS.

July 3, 1945. R. B. SCHAAL 2,379,659

REFINING OF COBALT ORES

Filed Dec. 24, 1940 6 Sheets-Sheet 5

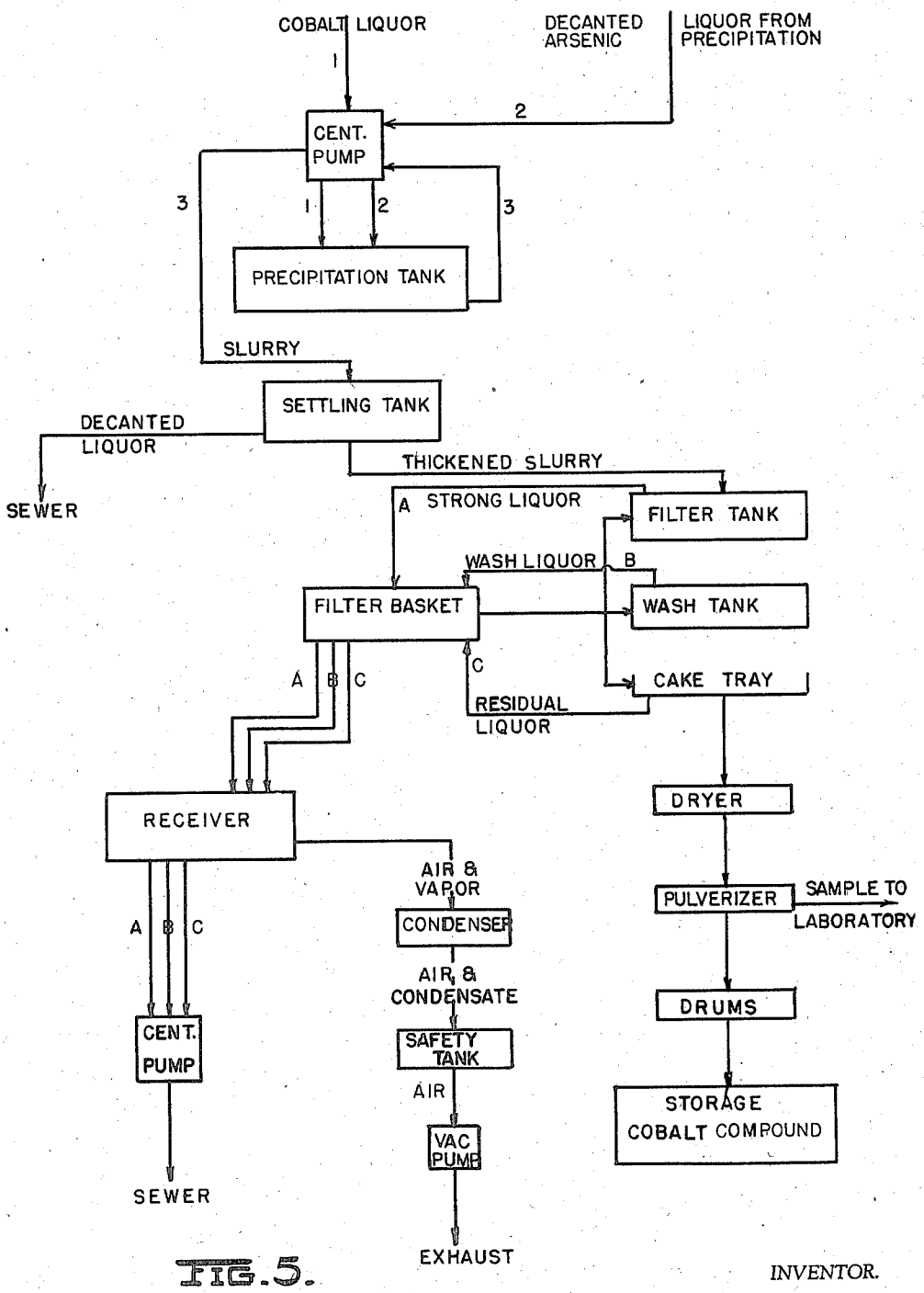

FIG. 5.

INVENTOR.
ROBERT B. SCHAAL
BY Oberlin, Limbach & Day
ATTORNEYS.

July 3, 1945. R. B. SCHAAL 2,379,659

REFINING OF COBALT ORES

Filed Dec. 24, 1940 6 Sheets-Sheet 6

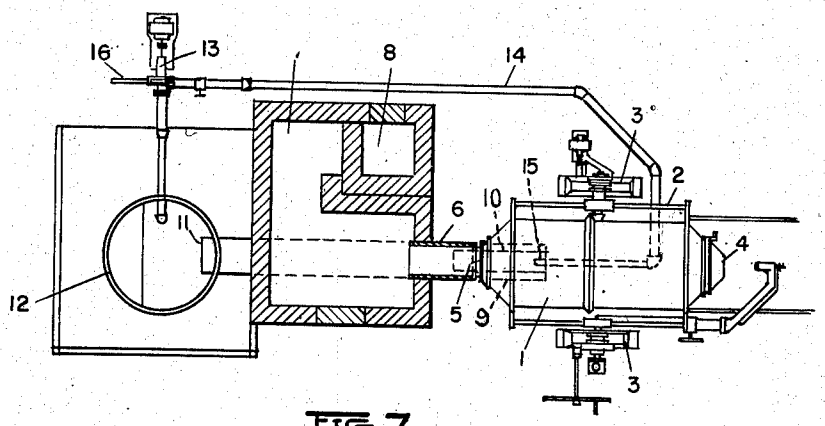

FIG. 7.

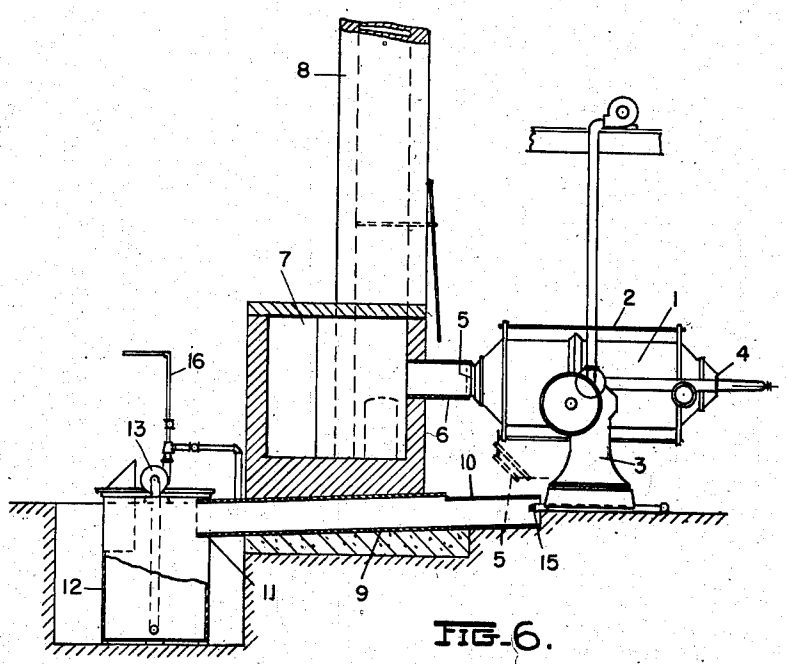

FIG. 6.

INVENTOR.
ROBERT B. SCHAAL
BY Oberlin, Limbach & Day
ATTORNEYS.

Patented July 3, 1945

2,379,659

UNITED STATES PATENT OFFICE

2,379,659

REFINING OF COBALT ORES

Robert B. Schaal, Independence, Ohio, assignor to Ferro Enamel Corporation, Cleveland, Ohio, a corporation of Ohio

Application December 24, 1940, Serial No. 371,509

14 Claims. (Cl. 75—82)

This invention relates to a process of refining cobalt ores.

The ores from which cobalt is obtained generally contain other metals, together with arsenic and/or sulphur, which, from the standpoint of obtaining cobalt, are regarded as impurities. Thus far in the refining of cobalt the presence of arsenic and sulphur in the ore has presented considerable difficulty with respect to separating these ingredients from the cobalt. The arsenic and sulphur must be completely removed since their presence renders the cobalt objectionable for use in the ceramic industry or for use in the preparation of enamel frits. The difficulty in refining the cobalt ore has been due to the fact that the ore contains metals such as iron and nickel which have properties similar to cobalt, and due to the fact that the nickel and cobalt directly combine quite readily with the sulphur and arsenic.

Heretofore the recovery of cobalt has usually started with smelting the ore in a blast furnace and in such case, the arsenic and sulphur was availed of to form a speiss or matte in which the cobalt and nickel would be present in the form of sulphides or arsenides. The usual process then involved treating the speiss or matte by grinding and roasting to remove the excess of arsenic or sulphur. The arsenic would pass off as arsenious oxide which could be recovered leaving the heavier metals as oxides. However, by this method it was impossible to remove all the arsenic and it was then necessary to treat the speiss by other methods to remove the arsenic and sulphur as impurities and separate out the cobalt and nickel. In treating cobalt ore in this way it is generally necessary to precisely control the amount of iron permitted to go into solution during the formation of the speiss or matte since the presence of some iron is necessary to enable the removal of the arsenic by wet methods employed subsequent to the grinding and roasting of the speiss to drive off excess arsenic. Moreover, during the roasting of the speiss it is generally necessary to exercise a rather precise control of the amount of arsenic driven off by roasting, since the presence of a certain amount of arsenic is necessary in order to enable the removal of the iron, the iron and arsenic assisting in the removal of each other and forming ferric arsenate upon the neutralizing of an acid solution of the ground and roasted speiss. Another reason for permitting iron to enter the speiss or matte is to minimize the loss of cobalt and nickel in the slag.

One of the principal objects of this invention is to provide a process for refining cobalt ore which is not dependent upon smelting the ore to form a speiss or matte and in which roasting is not necessary to separate the arsenic and sulphur from the cobalt.

A further object is to provide a process for refining cobalt ore in which the arsenic and sulphur are converted into soluble salts which are separated from the cobalt by lixiviation and recovered as a commercially valuable by-product.

A further object is to provide a process for refining cobalt ore in which the arsenic is recovered as a commercially valuable by-product and in which one of the products formed during the recovery of the arsenic may be employed in the recovery of the cobalt.

A further object is to provide a process for refining cobalt ore in which the ore is fused with other materials by the application of heat to form soluble salts of the arsenic and sulphur which may be removed from the ore by leaching and to convert the metal content of the ore into insoluble oxides.

My invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain steps embodying the invention, such disclosed steps constituting, however, but one of the various ways in which the principle of the invention may be used.

In the annexed drawings, Figs. 1 to 5 are flow sheets diagrammatically illustrating a plant layout of apparatus suitable for carrying out the various steps of the process of this invention. In this showing:

Figure 1 illustrates the arrangement of the apparatus by which the material is handled to form a fused mixture of the ore prior to separation of the sulphur and arsenic from the metallic materials.

Figure 2 illustrates the arrangement of the apparatus by which the fused material from the operation shown in Figure 1 is treated to separate the arsenic from the ore in the form of a liquor and to obtain the metals as a solid in the form of water insoluble oxides.

Figure 3 illustrates the arrangement of the apparatus by which the arsenic liquor obtained from the operation shown in Figure 2 is treated to obtain commercial calcium arsenate, together with sodium hydroxide as a by-product.

Figure 4 illustrate the arrangement of the apparatus by which the metallic oxides obtained from the steps shown in Figure 2 are treated to separate out certain of the metallic materials and to obtain the cobalt in the form of a liquor.

Figure 5 illustrates the arrangement of the apparatus by which the cobalt liquor obtained from the steps shown in Figure 4 is treated with the caustic liquor derived as a by-product from the steps shown in Figure 3 to obtain the cobalt in the form of the commercially available compound.

Figure 6 is a side elevational view, partially in section, of an alternative form of apparatus adapted to carry out the steps intermediate the

furnace of Figure 1 and the leaching tank of Figure 2.

Figure 7 is a top plan of the apparatus shown in Figure 6.

This invention, generally stated, comprises the steps of substantially completely separating the arsenic and sulphur from the ore for the purpose of converting the metal ingredients of the ore into insoluble oxides, treating the separated arsenic and sulphur material to recover the arsenic as a commercially valuable by-product, dissolving the metal oxides in acid to enable recovery of the cobalt and other metallic elements, and employing one of the products formed in the step of recovering the arsenic as an agent in the separating of the cobalt and other metals out of the solution.

More specifically, the process of this invention is started by crushing and pulverizing the cobalt ore which is then mixed with salt, soda ash and nitre. The amount of soda ash and nitre will in general be dependent upon the sulphur and arsenic content of the ore, the salt being added to enable the ore to be fused upon the application of heat in a manner to be described. For an ore containing 20% arsenic and 12% sulphur it has been found that a desirable mixture comprises 25% ore, 15% salt, 12½% soda and 47½% nitre. Since the range of arsenic and sulphur in commercially workable cobalt ores or concentrates is generally between 3% and 15% sulphur and between 18% and 35% arsenic, the range of mixtures of ore, salt, soda and nitre to form a fused mixture will in general be: ore 15% to 25%, salt 15% to 50%, soda 5% to 20% and nitre 20% to 50%.

The mixture of ore, salt, soda and nitre is then fused by the application of heat and during fusion the arsenic and sulphur is converted into sodium arsenate and sodium sulphate, all of the arsenic being converted into sodium arsenate, and the metallic ingredients are separated from the arsenic and sulphur and converted into insoluble oxides. The fused mixture is then introduced into a leaching tank wherein a slurry of water and the fused materials is formed. Thus slurry is then filtered and the soluble materials, sodium arsenate and sodium sulphate, are recovered as a filtrate which will be referred to as arsenic liquor. The non-soluble materials will be left behind as a cake consisting mostly of the metallic oxides of cobalt, copper, iron and nickel and varying amounts of other materials such as manganese, silica, alumina, magnesium and lime.

To the filtered solids which were separated from the arsenic liquor, a solution of 18° Baumé hydrochloric acid is added in excess and heated until all the metals in the filtered cake are dissolved. The hydrochloric acid dissolves everything but the gangue and silica which form a sludge. This mixture is then cooled to room temperature and added to a large excess of a cold emulsion of calcium carbonate while stirring the same. The addition of the calcium carbonate will cause the iron, lead, silica, arsenic if any is left, and other materials to be precipitated out of the solution as solid materials and only the cobalt, nickel, copper and manganese will be left in the solution as chloride salts. This mixture is then filtered and washed with water to separate out the solid materials and the filtrate and washing liquid which contain the metallic chloride salts in solution is saved. This recovered filtrate will now be referred to as cobalt liquor.

At this point, it will be noted that the process has resulted in the formation of two filtrates or liquors which have been referred to generally as arsenic liquor and cobalt liquor.

In the treatment of the arsenic liquor, the liquor is first heated and gradually introduced into a mixture of hot milk of lime. Since the arsenic liquor contains sodium arsenate, sodium sulphate, sodium chloride, and sodium carbonate in solution, the arsenic will be precipitated out as calcium arsenate together with some calcium carbonate. The reaction in this step also forms sodium hydroxide in solution which is recovered by decanting and employed in a manner to be described. The precipitate of calcium arsenate remaining is in the form of a slurry which is filtered to form a cake which is then washed, dried and pulverized, and thus recovered in a commercially valuable form. The hot milk of lime and arsenic liquor are heated prior to being intermixed in order that the calcium arsenate will be in a non-gelatinous form and more easily recoverable than would be the case if the solution of calcium hydroxide and arsenic liquor were intermixed while cold. The precipitate would be gelatinous and difficult to recover if these materials were intermixed in a cold state. The heat substantially dehydrates the solids precipitated out of the arsenic liquor.

The decanted sodium hydroxide obtained during the treatment of the arsenic liquor is then mixed with the cobalt liquor in proper proportions to obtain a pH of between 8.3 and 8.8. In this step the cobalt, nickel and some copper and manganese are precipitated out of the cobalt liquor in a form which may be termed basic or hydroxy-carbonates. It is important that the pH be maintained within the limits referred to, since if the pH is lower than 8.3 some of the cobalt will remain in solution, and if above a pH limit of 8.8 some of the calcium will be precipitated, thereby making the washing and drying of the precipitate difficult and also introducing impurities. The remaining liquor, containing calcium chloride, sodium chloride and sodium sulphate, together with other materials in solution, is decanted and filtered and the cobalt-containing residue is dried. This residue of metallic hydroxy-carbonates is dried at a temperature of 500° to 1000° F. until black, and the product thus obtained has an ignition loss of about 10% to 20%. In the product obtained by drying, the metals are present substantially in the following proportions: cobalt 40% to 50%, nickel 10% to 20%, copper 1% to 3%, manganese ½% to 2½%, together with lime as a chloride 0% to 2%, and the residue, iron, as an impurity, ½% to 1½%. The metals in this product may then be further separated out by known processes.

Apparatus

The various detailed steps of this invention will be best understood by reference to the drawings or flow sheets showing the arrangement of apparatus by which the process of refining cobalt ores may be reduced to commercial practice. The ore to be refined is preferably ore which has been treated to increase the cobalt content thereof by the removal of the gangue or other foreign materials. This ore may be obtained in its natural state or from the discard piles of cobalt-containing ore which has been subjected to other refining processes in the recovery of other metals or materials contained in the original ore.

As shown in Fig. 1, the ore, soda, nitre and salt is delivered to the plant and dumped into

separate piles. The soda, nitre and salt are then carried by bucket elevators to separate compartments of a four-compartment storage bin. The ore is delivered to a feed bin and then taken to a pulverizer where it is crushed and ground to a size of about 40 mesh and is then taken through the mixer to the fourth compartment of the four-compartment storage bin. The materials from the storage bin are delivered in pre-calculated quantities in the proportions as set forth above to a weighing hopper and thence to a mixer where the materials are thoroughly mixed prior to being taken to a furnace charger for delivery to a furnace which is preferably of the rotary type. The material, after being delivered to the furnace, is subjected to a temperature of from 1200° to 1300° F. which fuses the materials into a liquid mass. The liquid melt or fused materials is then delivered onto a water-cooled, cast-iron hearth where the fusion solidifies and is then broken up and taken to a crusher. From the crusher, the fused materials are taken through a pulverizer wherein the fused material is pulverized to a size of about 40 mesh and is thence delivered to a storage bin for further operations.

Referring to Figure 2, the pulverized, fused material from the storage bin of Figure 1 is taken to a weighing hopper from which it is fed to a leaching tank provided with a portable mixer. In the leaching tank, the water dissolves the arsenic and sulphur compounds and other soluble materials out of the fused mixture and this solution forms a slurry with the remaining insoluble metallic oxides. The slurry is then taken to a filter tank wherein the filtrate which has been referred to as arsenic liquor is recovered. The solids are then washed in a wash tank and then delivered to a cake tray wherein the insoluble oxides are collected. From the caking tray, the solids are taken to a bin prior to being introduced into a dissolving tank in a manner to be described. The filtrate recovered from the slurry formed in the leaching tank is taken to a storage tank. The liquids B, C and D, respectively recovered from the wash tank, cake tray and condensing apparatus, are not delivered to the arsenic storage tank but are taken to a separate storage tank for use in connection with subsequent leaching of additional fused material in order to concentrate the arsenic content of the liquor A taken to the arsenic storage tank.

In Figs. 6 and 7, there is shown an alternative and preferred arrangement of apparatus for forming the slurry of metallic oxides and arsenic liquor. In this showing, the numeral 1 indicates a rotary furnace mounted on a carriage 2 for rotational movement with respect thereto about its horizontal axis. The carriage 2 is provided with trunnion arms rotatably mounted in supports 3 to permit tilting movement of the carriage 2 and furnace 1 carried thereby from its horizontal charging and heating position to an inclined discharging position indicated partially by broken lines as shown in Fig. 6. The furnace 1 is provided with a charging opening 4 at one end thereof through which the materials adapted to form the fused mixture may be fed in proper proportions as by means of a suitable screw conveyor. The other end of the furnace 1 is provided with an opening 5 through which the exhaust gases may escape and through which the liquid fusion melt may be discharged at the end of a heating operation. When the furnace is in its horizontal heating position, the opening 5 has communication with a conduit 6 through which the exhaust gases may be conducted to the expansion chamber 7 which in turn is connected to an exhaust stack 8.

An inclined conveyor pipe 9 is provided with an opening 10 adjacent one end thereof underneath the furnace discharge opening 5 for a purpose to be described. The other end 11 of the pipe 9 has communication with a leaching tank 12. The leaching tank 12 is provided with a circulating pump 13 and circulating line 14 for pumping water from the tank 12 to a nozzle 15 located at one end of the pipe 9 under the opening 10. The water pumped to the nozzle 15 will be returned in a continuous stream to the tank 12 through the pipe 9.

After a charge of ore, soda, salt, and nitre is placed in the furnace 1 and fused by the application of heat, the pump 13 is started to circulate water from the tank 12 through the pipe 9. The furnace is then tilted to the position indicated in dotted lines, and the liquid melt of fused materials flows out of the discharge opening 5 and through the opening 10 into the pipe 9. Upon contacting the stream of water flowing through the nozzle 14 and pipe 9, the liquid melt will be solidified and broken up into small particles and will be carried by the water to the leaching tank 12. The soluble materials of the fused mixture will dissolve in the water to form the arsenic liquor and metallic oxide slurry as explained above. After the materials have been recirculated through the tank 12 a sufficient length of time, the pump 13 may be employed to pump the slurry from the tank 12 through a pipe 16 to a filtration tank. By this apparatus, the cooling, crushing, and pulverizing operations diagrammatically illustrated in Fig. 1 are eliminated.

In connection with the apparatus shown in Figs. 6 and 7, it will be understood that suitable controls (not shown), for preventing the discharge of the furnace 1 unless sufficient water to prevent damage is flowing through the pipe 14 and nozzle 16, are provided. It will also be understood that the capacity of the tank 12 and pump 13 will be large enough to supply water to the pipe 9 in an amount sufficient to prevent damage due to too rapid a generation of steam.

Referring to Fig. 3, the arsenic liquor A obtained from the operations illustrated in Fig. 2 is taken to a steam coil heated storage tank from which it is delivered under controlled conditions to a precipitation tank containing a hot slurry of calcium hydroxide. The slurry of calcium hydroxide is produced by slaking a measured quantity of calcium oxide with hot water. All the material from the precipitation tank is transferred to a decantation tank where the precipitate is permitted to settle in order that the supernatant liquor may be decanted. This decantation operation is repeated twice. This decantation serves two purposes; first, the precipitate is partially washed and, second, the whole slurry is cooled sufficiently to permit easy vacuum filtration. The decanted liquors from these operations have been respectively indicated as A, B and C. Liquor A contains a considerable quantity of sodium hydroxide in solution. Only the caustic liquor A is saved for subsequent use in a manner to be described. The slurry from the last decanting and settling operation is then taken to filter tanks and the solids recovered. The solid material is then pulverized, placed in bags and stored. This material is commercial cal-

cium arsenate of a character to be described below.

Referring to Fig. 4, the solid material obtained from the filtering operation shown in Fig. 2 is taken to a steam heated dissolving tank wherein it is dissolved in a hot solution of 18° Bé. muriatic acid. This solution is then conducted to a precipitation tank where it is slowly mixed with a slurry of calcium carbonate. This slurry is made by agitating a weighed quantity of whiting in cold water. This step causes the precipitation of certain materials in a manner to be described, and the slurry of precipitated solids and liquid is taken first to a filtering tank where the solids are separated from the liquor. The filter leaves with their adhering solids are transferred to a wash tank where the last traces of mother liquor are removed and then the solids, composed of basic iron carbonate, silica and other waste products are discarded. The liquors A from the filter tank and B from the wash tank and C from the cake tray are pumped to a storage tank. This liquor contains the cobalt in solution and has been referred to as cobalt liquor.

Referring to Fig. 5, the cobalt liquor obtained from the operation shown in Fig. 4 is introduced into a precipitation tank together with the caustic liquor obtained as a by-product during the recovery of the calcium arsenate in the operation shown in Fig. 3. The caustic liquor causes the cobalt and other materials to be precipitated in a manner to be described. The slurry of precipitated materials from the precipitation tank is then pumped to a settling tank from which some of the resultant liquor is decanted. The thickened slurry is then filtered, washed and caked and the liquors A, B and C from these operations are removed and discarded, as shown. The cake solids are then taken to a drier for a drying operation and thence to a pulverizer prior to being stored. The pulverized material is a commercially valuable cobalt bearing material of a character to be described.

Chemical reactions

Due to the complex nature of the materials contained in the ore and the fact that it is practically impossible to define chemically the structure of such materials, the chemical reactions which take place in the various steps of this invention are of necessity based upon assumed conditions, which, although not inaccurate, cannot be said to represent the conditions as they actually exist. Accordingly, it will be understood that the discussion below, of the chemical reactions is intended as only generally representative of what actually takes place, and is given for the purpose of enabling a better understanding of this invention to be had.

The step of fusing the ore with salt, soda and nitre converts the arsenic and sulphur into a state where the arsenic can be readily recovered in a commercially valuable form, and enables the sulphur and arsenic to be separated from the remaining constituents of the ore. In this step, the salt is not believed to enter into the chemical reaction which takes place during the fusion. The addition of the salt enables the mixture to fuse and become fluid quite readily at a comparatively low temperature. The fusion becomes sufficiently fluid at a temperature of about 1200°–1300° F., which is considerably lower than would be required if the salt were not added. Without the salt, in addition to requiring a much higher temperature to effect a fusion-like condition of the ore, soda and nitre, it has been found practically impossible to effect a satisfactory fluid-fusion condition of the material regardless of the temperature employed.

In the fusion of the ore under strongly basic and oxidizing conditions, the arsenic and sulphur are oxidized to the pentavalent and hexavalent conditions respectively, and on leaching with water yield a solution of sodium arsenate and sodium sulphate. The fusing step chemically separates the arsenic and sulphur from the metal constituents of the ore. The leaching physically separates the arsenic and sulphur from the metal constituents of the ore. After leaching, the metals are left as insoluble residues, in their highest state of oxidation and probably somewhat hydrated. Using cobalt as an example, the metallic oxides may be represented as $Co_2O_3.xH_2O$.

The ore consists of a number of indefinite metallic arsenides, sulphides and/or sulpho-arsenides, the metals being principally cobalt, nickel, iron, copper and manganese. From its highly indefinite and complex state, it is impractical to determine and impossible to state the exact compounds of which the ore is composed, and therefore, to determine exactly the original valence or degree of oxidation of the elements present. For the purpose of calculating the fusion mixture, it has been assumed that each element is present in its uncombined or elementary state. The calculation thus reduces to the following probable reactions, using cobalt as the representative metal and treating all the metals alike in the calculation:

(1) $6As+10NaNO_3+4Na_2CO_3 \rightarrow 6Na_3AsO_4+10NO+4CO_2$

(2) $S+2NaNO_3 \rightarrow Na_2SO_4+2NO$

(3) $2Co+2NaNO_3 \rightarrow Co_2O_3+2NO+Na_2O$

The uncombined Na_2O remaining in Reaction 3, very likely replaces that furnished by the Na_2CO_3 indicated in Reaction 1 so that in calculating the mix this probability is assumed to be a certainty and proper adjustment is made.

The reactions of the other metals are assumed to follow the pattern represented in Equation 3.

The gangue or silicious and aluminous materials in the ore are very probably partially converted during the fusion to alkali silicates, which in turn partially break down or hydrolyze on leaching with water.

The filtrate, or arsenic liquor obtained after leaching the fused mixture consists principally of a solution of sodium arsenate (Na_3AsO_4), sodium sulphate (Na_2SO_4), sodium chloride (NaCl) and sodium carbonate (Na_2CO_3).

The residue consists principally of the metals, silica and alumina, probably in the following representative conditions:

Cobaltic oxide, partially hydrated ($Co_2O_3.xH_2O$)
Nickelic oxide, partially hydrated ($Ni_2O_3.xH_2O$)
Ferric oxide, partially hydrated ($Fe_2O_3.xH_2O$)
Cupric oxide, partially hydrated ($CuO.xH_2O$)
Manganic oxide, partially hydrated ($Mn_2O_3.xH_2O$)

and/or

Manganese dioxide, partially hydrated ($MnO_2.xH_2O$)
Silica ($SiO_2.xH_2O$)
Alumina ($Al_2O_3.xH_2O$)

In addition, the residue probably contains small

amounts of most or all of the elements, lead, calcium, magnesium and silver, in similar form.

As pointed out heretofore, the arsenic liquor is heated, and run into a hot slurry of milk of lime, in calculated quantity to precipitate the arsenic as a "calcium arsenate" of controlled composition and properties. Due to the presence of some carbonate both in the quicklime from which the slurry is made and in the arsenic liquor, a certain amount of calcium carbonate, indefinite, but capable of control, is precipitated along with the arsenate. The calcium arsenate also contains water of hydration, the amount of which is controlled by the conditions of precipitation. Commercial calcium arsenate contains about

	Percent
CaO	42–44
As_2O_5	40–42
CO_2	2–4.5
H_2O	10–14

The milk of lime and arsenic liquor mixture is calculated to give a precipitate having a composition substantially that of the commercial calcium arsenate set forth above, and such composition may be represented by the hypothetical formula of $4CaO.As_2O_5.3H_2O+xCaCO_3$ as an impurity. The sulphate in the arsenic liquor is not precipitated to an appreciable extent. The reaction in addition to precipitating calcium arsenate also gives sodium hydroxide which is decanted off and recovered as a filtrate. The reaction of the arsenic liquor with boiling milk of lime may be set forth as follows:

(4) $2Na_3AsO_4+4Ca(OH)_2+2H_2O\rightarrow 4CaO.As_2O_5.3H_2O+6NaOH$

The residue of metallic oxides obtained after leaching the pulverized fused mixture is then dissolved in hot muriatic acid to convert the metals to soluble chlorides. This reaction may be given as follows, using cobalt as the representative metal.

(5) $Co_2O_3.xH_2O+6HCl\rightarrow 2CoCl_2+(x+3)H_2O$

The silica and alumina partly dissolve. To separate out the silica, alumina, iron, etc., the solution of metallic chlorides after cooling is then poured into an emulsion of calcium carbonate in excess. This precipitates the elements such as silica, alumina, iron, and leaves the cobalt, nickel, copper and manganese in solution as chlorides along with a large amount of calcium chloride, which is formed by the muriatic acid reacting with the calcium carbonate. The pH of the solution after precipitation is 4.5 to 6.0, indicating various degrees of saturation of the solution with CO_2. It is important to keep the saturation of Co_2 high so that no cobalt and nickel precipitate.

The precipitate formed by this reaction is not clear cut and definite in composition, but consists principally of silica, alumina (either as hydrate or calcium salt or both), and a rather complex indefinite hydrated carbonate of iron. Since the reaction products in precipitating out the iron etc. are not capable of exact chemical definition, the reaction may be indicated only generally as follows, using iron as the representative metal.

(6) $CaCo_3+2HCl\rightarrow CaCl_2+H_2CO_3$

(7) $FeCl_3+3H_2CO_3\rightarrow Fe(HCO_3)_3+3HCl$

The excess calcium carbonate added neutralizes the HCl formed in Reaction 7.

After filtration and thorough washing, the precipitate obtained upon addition of the acid solution of metallic chlorides to the excess of calcium carbonate, (as in Reactions 6 and 7), is discarded, and the filtrate and wash liquors, which have heretofore been referred to as cobalt liquor are saved. To this liquor is added the sodium hydroxide or caustic liquor obtained during precipitation of the calcium arsenate. The caustic liquor is added until a pH of 8.3 to 8.8 is obtained as described above.

The cobalt liquor and caustic liquor contain the following principal materials:

Cobalt liquor	Caustic liquor
Cobalt chloride ($CoCl_2$)	Sodium hydroxide ($NaOH$)
Nickel chloride ($NiCl_2$)	Sodium sulphate (Na_2SO_4)
Copper chloride ($CuCl_2$)	Sodium chloride ($NaCl$)
Manganese chloride ($MnCl_2$)	Sodium carbonate (Na_2CO_3)
Calcium chloride ($CaCl_2$)	
Carbon dioxide (CO_2)	

When the two liquors are united in the proper proportions the cobalt, nickel, copper and manganese are precipitated probably as mixed hydrates or hydrated carbonates, leaving the remaining constituents in solution. The precipitate is filtered off, washed, dried and pulverized and is ready for use. The reaction between cobalt chloride and sodium hydroxide may be represented thus:

(8) $CoCl_2+2NaOH\rightarrow Co(OH)_2+2NaCl$

It will be observed that the above described process comprising my invention is distinguishable over the prior art largely in the preliminary treatment given to the ore, in that all of the arsenic contained therein is preserved and ultimately recovered as an end-product of the process. In this particular, the present process is entirely different from those in which the ore in the preliminary stages of its processing has been heated to a temperature sufficiently high to liberate at least some of the arsenic even though such prior art processes in their initial stages attempted to convert the arsenic into an oxidized form. In my process the fusion is carried on at such a low temperature and under such strongly basic and oxidizing conditions as to prevent the undesirable features of the prior art set forth above.

The use of a fusion bath for the ore containing the constituents named gives rise to a number of advantages which may be partially enumerated as follows. In this connection, the proportions given in the specification herein are also important. The first desirable condition accomplished by the fusion as described is the complete retention of all the arsenic in the melt, thus enabling its complete final recovery in one operation and elimination of bag-houses or other precautionary measures to catch noxious fumes from the smelting. The second advantage peculiar to this particular treatment is also twofold and has to do with the relation between the speed of reaction and the fluidity of the fused mass. The fusion as described in the specification permits the production of a free flowing melt in which reactions can take place completely and easily and at the same time without danger of explosion or other such hazards. It is possible to produce a fluid oxidizing melt by the use of nitre and soda ash alone in certain proportions, but where the proportion of nitre is sufficiently high to accomplish the desired complete retention of

the arsenic and complete reaction, these reactions are apt to take place with explosive violence whereas if the proportion of soda ash is sufficient to prevent undesirable speed of reaction, the reaction is either incomplete or takes place at a temperature which is too high to be practical. The sodium chloride in the mixture serves as a diluent to the extent that it slows down the reaction sufficiently to eliminate hazard and at the same time preserves all the advantages to be gained by the high fluidity at low temperatures before mentioned.

The further use of the proportions of sodium chloride recommended herein becomes apparent when the method of recovery of the arsenic is considered. The arsenic is recovered as calcium arsenate and must be in a thoroughly pure state in order to be commercially marketable. If large quantities of sodium carbonate were to be used in the fusion mixture, the resulting calcium arsenate would inevitably be so contaminated with carbonate as to preclude commercial use. By the use of sodium chloride in place of certain quantities of sodium carbonate, the presence of excessive amounts of carbon dioxide is avoided and the recovery of calcium arsenate is made commercially practicable, by eliminating coprecipitation of undesirable amounts of calcium carbonate.

From the foregoing, it will be apparent that there is provided a novel method of refining cobalt ore in which the sulphur and arsenic, present as impurities, are first completely separated from the metal constituents without the necessity of smelting in a blast furnace, or the grinding and roasting required in the refining of cobalt ore as usually practiced. The process of this invention, beginning with forming the fused ore mixture, enables the arsenic and metals to be divided into separate phases which are dealt with individually in a simplified manner. It will be noted also that one of the by-products obtained in the treatment of the arsenic is used in the treatment of the metals. The manner in which the separate phases are treated provides a simplified process of refining arsenical cobalt ore at a minimum of expense.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the steps herein disclosed, provided those stated by any of the following claims or the equivalent of such stated means be employed.

I therefore particularly point out and distinctly claim as my invention:

1. In a method of refining cobalt ore, the steps which comprise forming a mixture of the ore with salt, soda, and nitre, and subjecting such mixture to a temperature of from about 1200° F. to 1300° F. to fuse the same.

2. In a method of refining cobalt ore containing from about 3% to 15% sulphur and from about 18% to 35% arsenic, the steps which comprise forming a mixture of ore 15% to 25%, salt 15% to 50%, soda 5% to 20%, and nitre 20% to 50%, and fusing such mixture by the application of heat thereto.

3. In a method of refining cobalt ore containing from about 3% to 15% sulphur and from about 18% to 35% arsenic, the steps which comprise forming a mixture of ore 15% to 25%, salt 15% to 50%, soda 5% to 20%, and nitre 20% to 50%, and subjecting such mixture to a temperature of from about 1200° F. to 1300° F. to fuse the same.

4. The method of separating arsenic and sulphur out of cobalt containing ore which comprises forming a mixture of the ore with salt, soda, and nitre, and subjecting such mixture to a temperature of from 1200° F. to 1300° F. to fuse the same.

5. The method of separating arsenic and sulphur out of cobalt containing ore which comprises forming a mixture of the ore with salt, soda, and nitre, fusing such mixture to form water soluble salts of the sulphur and arsenic, and water insoluble oxides of the metallic ingredients, removing and recovering said salts as a filtrate, and adding calcium hydroxide to said filtrate to precipitate the arsenic in the form of calcium arsenate.

6. The method of refining cobalt ores containing sulphur and arsenic which comprises treating the ore to obtain water soluble salts of the sulphur and arsenic, and water insoluble oxides of the metallic ingredients, removing and recovering said salts as a filtrate, adding said filtrate to hot milk of lime to obtain calcium arsenate as a precipitate and a liquor containing sodium hydroxide, forming a second solution of said oxides in muriatic acid, adding said second solution to an excess of an emulsion of calcium carbonate to precipitate some of the metals out of solution as impurities, filtering said second solution to remove said precipitated impurities, and adding said liquor containing sodium hydroxide to said filtered second solution to precipitate the cobalt out of solution.

7. The method of refining cobalt ores containing sulphur and arsenic which comprises forming a mixture of the ore with salt, soda, and nitre, fusing said mixture to obtain water soluble salts of the sulphur and arsenic, and to obtain the metallic elements in their oxidized form, removing and recovering said salts as a filtrate, adding said filtrate to hot milk of lime to obtain calcium arsenate as a precipitate and a caustic liquor containing sodium hydroxide, forming a second solution of said oxides in muriatic acid, adding said second solution to an excess of an emulsion of calcium carbonate to precipitate some of of the metals out of solution as impurities, filtering said second solution to remove said precipitated impurities, and adding said caustic liquor containing sodium hydroxide to said filtered second solution to precipitate the cobalt out of solution.

8. The method of refining cobalt ores containing sulphur and arsenic which comprises fusing said ore under strongly basic and oxidizing conditions, and adding said fusion to water to form a slurry.

9. The method of refining cobalt ores containing sulphur and arsenic which comprises fusing said ore to form water soluble salts of the arsenic and sulphur, and water insoluble oxides of the metallic ingredients, and leaching said fusion by introducing the same while in hot liquid form into a flowing stream of water.

10. In the method of refining cobalt ores, the step of leaching out the water soluble salts of arsenic and sulphur, which comprises forming a liquid fusion of the ore, and introducing such fusion while hot into a flowing stream of water.

11. In a method of refining cobalt ore, the step which comprises heating a mixture of ore, soda, and nitre, with sufficient salt to enable the production of a free flowing melt, at temperatures not substantially in excess of about 1300° F.

12. In a method of refining cobalt ore, the

step which comprises heating a mixture of ore, soda, and nitre, with sufficient salt to enable the production of a free flowing melt, in which the arsenic content of the ore is completely retained.

13. In a method of refining cobalt ore, the step which comprises heating a mixture of ore, soda, and nitre, with sufficient salt to enable the production of a free flowing melt, in which the arsenic content of the ore is completely retained, at temperatures not substantially in excess of about 1300° F.

14. In a method of refining cobalt ore, the step which comprises heating a mixture of ore, soda, and nitre, with sufficient salt to enable the production of a free flowing melt.

ROBERT B. SCHAAL.