Aug. 2, 1938. G. E. BEHR 2,125,329

REFINING METAL

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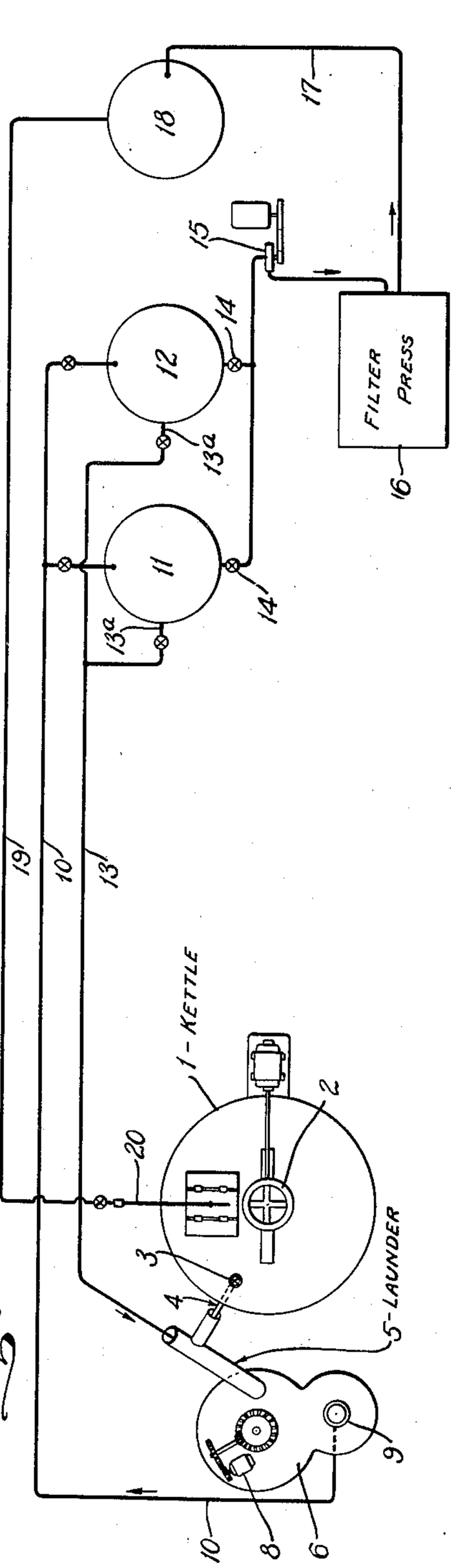

Fig. 1

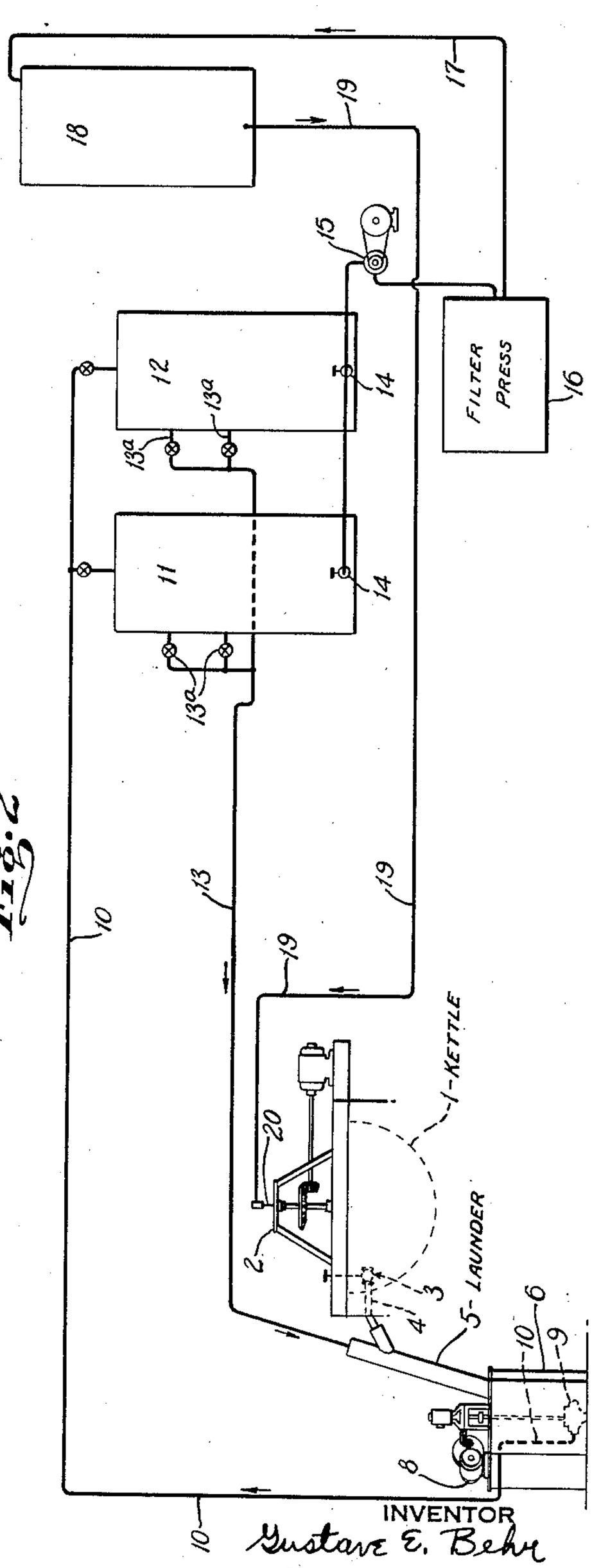

Fig. 2

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REFINING METAL

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6 Claims. (Cl. 75—78)

The invention relates to processes for the treatment of metals with water soluble reagents, for instance, caustic alkali, and in which steam is employed in reactive relation, or in which its presence is permissible. More particularly it relates to and is a development of the process disclosed in Dittmer Patent 1,976,333 for the selective removal from lead, or from lead-antimony alloys, of tin, arsenic, etc. The object is the simplification of processes of this general character and of the Dittmer process in particular, and the invention is described below in connection with the latter, though without limitation thereto.

In the Dittmer process, the lead alloy from which the selective removal is to be made, is melted and then treated conjointly with molten sodium hydroxide and steam, resulting in the production of oxysalts of the tin and of the arsenic if present, which are taken up in the molten caustic mass while the lead, or lead and antimony as the case may be, are relatively unaffected and remain in the metal bath. The steam promotes the reaction and, under proper temperature control, lends a high degree of selectivity to the process as between tin and arsenic on the one hand and the lead and antimony on the other, as pointed out in the Dittmer patent.

The Dittmer and other caustic treatment processes are not commercially practical unless the soda and the values in the oxysalts can be easily recovered. The usual procedure is to remove the salt-laden caustic mass from the kettle and treat it or mix it with water which dissolves the soda and any other solubles, such as sodium nitrate if that has been used, with the soda. After metallic particles carried in the mass have been separated, the mixture is then concentrated to a certain gravity, and cooled to a certain temperture, whereupon any insolubles and crystallized sodium or other salts are precipitated and removed, after which the remaining solution is evaporated to dryness and the soda stored to be used over again in the kettle. The separated metal is returned to the kettle.

By this invention the reclamation part of processes of this kind is substantially simplified and its cost reduced, including cost for equipment as well as operating cost, and in addition certain practical advantages are obtained as will presently become apparent.

In the accompanying drawing the invention is illustrated in diagram, Fig. 1 being a general plan and Fig. 2 an elevation of suitable equipment.

Assuming that the metal to be refined is an alloy of lead, antimony and tin with perhaps some arsenic and from which the tin and arsenic are to be removed, as contemplated by the Dittmer process, it is melted in a suitable kettle such as indicated at 1 and therein treated simultaneously with steam and caustic alkali, preferably sodium hydroxide, under vigorous vortical stirring, as by means of a power stirrer, indicated generally by 2, mounted on or over the kettle. Such vortical stirrers are well known in the art and do not need illustration. Under the proper conditions practically all of the tin and arsenic are presently oxidized and taken up by the caustic mass which in consequence gradually becomes thicker.

When such mass has accumulated a quantity of sodium salts but not so much as to make it non-fluid, the stirring is stopped and some of it is drawn off, or allowed to flow off from the surface of the metal on which it is floating, through a cock or valve 3 and a conduit 4 to a launder 5 and thence to a receptacle 6. The outlet through the cock 3 will be understood to be located at an appropriate level for this purpose, above the metal level and below the caustic level and more than one can be provided, at different levels, if desired though only one is indicated. In any case the cock or cocks are desirably located inside of the kettle and the conduit 4 passes through the kettle wall, so that those parts are subject to the kettle heat and thereby kept from becoming plugged with congealed caustic. Obviously the caustic could be removed by ladle but the outflow system just described provides convenience and speed. Preferably, not enough of the caustic is removed from the kettle to prevent immediately continuing the treatment of the metal in the kettle, more caustic being added to replace that withdrawn, as later explained.

In the pipe 5 or launder, the molten soda mass encounters aqueous liquor or water entering from a pipe 13 by which it is instantly disintegrated and the salts brought into solution or suspension. Depending on the metals constituting the alloy under treatment and the particular reagents used there may be more or less insoluble salts in the caustic mass, for instance, sodium stannate. Numeral 8 represents motor-driven stirring mechanism in receptacle 6 to maintain the suspension and 9 represents a motor-driven transfer pump, which is indicated as submerged in the liquid but which can be arranged elsewhere in the system if desired.

By the operation of this pump, the solution or suspension is discharged, through a pipe 10 to

the upper part of one or the other of two settling tanks 11 and 12, which may be duplicates of each other and which are connected in the system by appropriate valve connections as indicated so that they can be used alternately. In the tank which is connected in service, opportunity is provided for the launder liquid to drop its solid matter, such solids including the salts which have crystallized as well as the insolubles, all of which accumulate as sludge in the bottom of the tank. The relatively clear liquid above the sludge is taken off, by gravity flow or otherwise, by the pipe 13 above referred to and returned to the launder and receptacle 6, there to take up further soda and salts, in a circulatory manner. The pipe 13 is shown as having several connections 13a to each settling tank at graded levels in order to facilitate removal of clear liquid above the rising sludge level as the tank fills. A perfect separation of the solids is not necessary since the action is cumulative.

The circulation between the launder 5 and the settling tank is more or less continuous, and the accumulation of solids in the connected tank can be allowed to continue until the liquid from the upper part is so thick with salts dissolved or suspended that it will just flow in the pipes. At such time and without reference to the attainment of any particular gravity or temperature, the tank is shut off from the circulation and its contents evacuated through the bottom cock 14 and delivered by a pump 15 to a filter press indicated generally by 16. In this press the solids are collected in the form of a filter cake and the clear liquor, which is essentially a solution of caustic soda, is discharged by pipe 17 to the storage tank 18.

From this tank it is withdrawn continuously or as needed by pipe 19 and delivered by the hose or pipe 20 at the end of the latter into the treating kettle 1 to which it thus returns the soda previously removed, while the steam resulting from the evaporation of the water of the solution on contact with the contents of the kettle, either escapes inactively to the ventilation system (not indicated) or serves as the companion reagent with the soda as in the Dittmer process. Except for the soda chemically combined and that entrained in the filter cake it is all returned to the kettle in the form of solution and more is of course added from time to time to make up for losses. To the extent that the soda mass may gradually accumulate salts or compounds which do not readily precipitate in the settling tanks, it can of course be treated for their removal from time to time but no such accumulation occurs in working on the ordinary run of secondary metals.

As a particular advantage of the process it may be noted that the removal of the molten caustic from the kettle while still fluid, is not only rapidly accomplished but automatically prevents the transfer to the launder of any kettle metal in the form of prill and thereby entirely eliminates the metal separation step necessary in the caustic alkali process as heretofore practiced, as well as the special apparatus required for it. When as heretofore customary, the soda is used in the kettle until it is so stiff it cannot longer be stirred into the metal, it carries with it a considerable quantity of prill which has to be separated, whereas by removing the mass while still too thin to suspend the prill, that is to say, while so thin that metal particles in it drop instantly back into the metal bath underneath, separation occurs in the kettle itself and substantially no metal is carried off, which fact represents a material saving.

The filter cake derived from the press contains the oxysalts of the metals removed from the kettle and, depending upon what they are, may be recovered in various ways. In the case of the removal of tin only from the kettle metal, the filter cake is largely sodium stannate, which can be sold as such, or electrolyzed to metallic tin or smelted with lead dross to make solder stock.

It will be apparent from the foregoing disclosure that by avoiding the costly step of reclaiming the soda in solid or dry form, as heretofore customary, the alkali treatment of metals is materially simplified and cheapened and further, that it is immaterial to the substantive invention what the nature or composition may be of the metals under treatment or the purposes of the treatment or the precise sequence of the steps, or the design of the apparatus, various modifications and adaptations of the process being obviously capable of employment without departing from the scope and spirit of the invention.

The invention includes further, as a particular improvement on the Dittmer process, the delivery of the water or the return of the soda liquor directly into the throat of the deep vortex created by the stirrer in the treating kettle. Whereas it might be assumed and has heretofore been taken for granted that water introduced in liquid phase into the kettle of molten metal must be carefully directed onto the surface only of the melt in order to be there converted into steam and avoid explosions from confined evaporation below the surface, I have found that this is not necessary and that by pointing the stream from the hose 20 directly into the center of the vortex the resulting steam, though produced under the surface, is utilized without explosive effect and further that by so doing the production rate of the process is materially increased. This central or sub-surface introduction of the returned soda liquor therefore characterizes the preferred form of the new process.

I claim:

1. In the process of treating molten alloys of the kind in which an alloy-component is reacted upon by a molten, water soluble reagent for the removal of such alloy-component, the improvement which consists in maintaining a circulation of an aqeous solution in a closed circuit, transferring the molten reagent from the kettle and depositing it in said circulation, separating accumulated solids from such solution and drawing off some of such solution and returning it to the kettle for further treatment of alloy.

2. In the process of treating molten alloys of the kind in which an alloy-component is reacted upon by a molten, water soluble reagent for the removal of such alloy-component, the improvement which consists in maintaining a circulation of an aqueous solution in a closed circuit, transferring the molten reagent from the kettle while it is still thin enough not to hold metallic prill in suspension in it and depositing such molten reagent in said circulation, allowing the solids in such solution to accumulate in a suitable chamber, removing and filtering such accumulated solids and delivering the filter liquor containing dissolved reagent to the treatment kettle.

3. Apparatus for the caustic alkali treatment

of metals comprising a treating kettle, a conduit thereon constituting a molten caustic overflow therefrom, and a launder receiving caustic from such overflow, in combination, with means including a settling tank for circulating water through said launder and tank and a pipe conducting liquid from said circulating means to said kettle.

4. Apparatus of the kind described, comprising a treating kettle, a conduit thereon constituting a molten caustic overflow therefrom, and a launder receiving caustic from such overflow, in combination with a circulating pipe system including said launder and including also a settling tank, means for separating the liquor from the settlings in said tank and a pipe for conducting such liquor to said kettle.

5. The process of treating molten lead alloys with caustic soda which consists in transferring the molten soda, while carrying the products of its reaction with alloy ingredients, from the treatment kettle and mixing it with water, separating solids from such water and feeding such water and the soda in solution therein into the treatment kettle for continuing the caustic treatment of the alloy.

6. The process of treating molten lead alloys with caustic soda which consists in transferring molten soda from the treatment kettle while it is still thin enough to flow freely and let any metallic prill therein drop out of it, mixing water with such transferred molten soda in a suitable receptacle, circulating the water-soda mixture from said receptacle through one or more sedimentation tanks and back to said receptacle, filtering out the accumulated solids in said tank and delivering the separated filter liquor into the treatment kettle to serve as caustic supply.

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