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PROCESS FOR THE DECOMPOSITION OF
METAL SALTS TO FORM OXIDES
Filed Feb. 20, 1941

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2 Sheets-Sheet 1

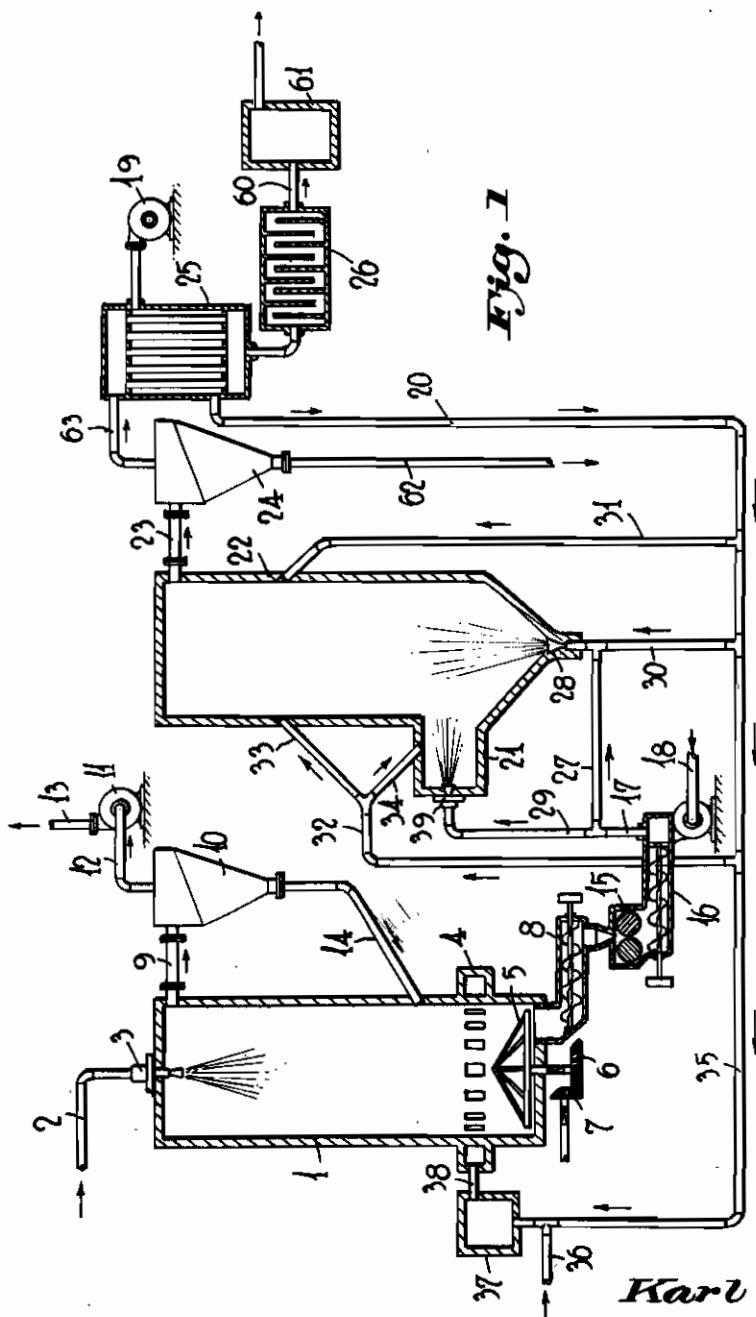


Fig. 1

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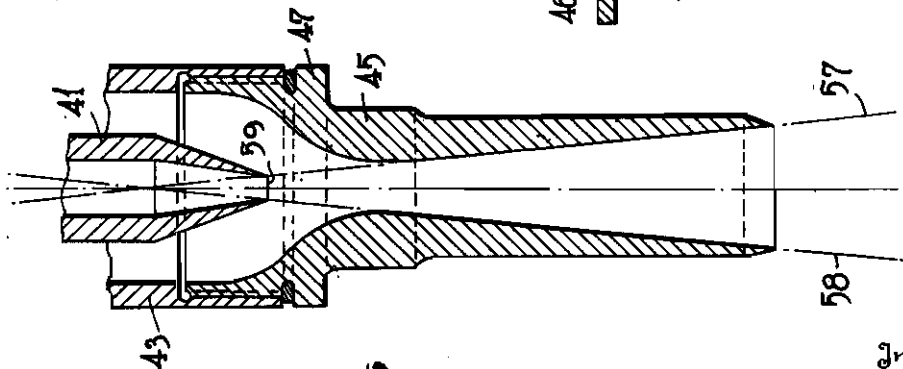
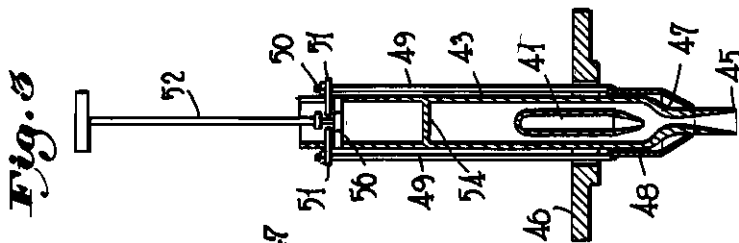
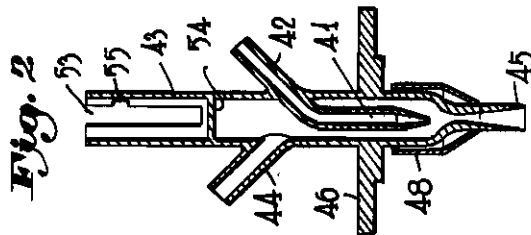
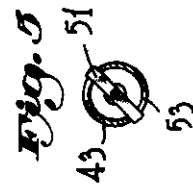
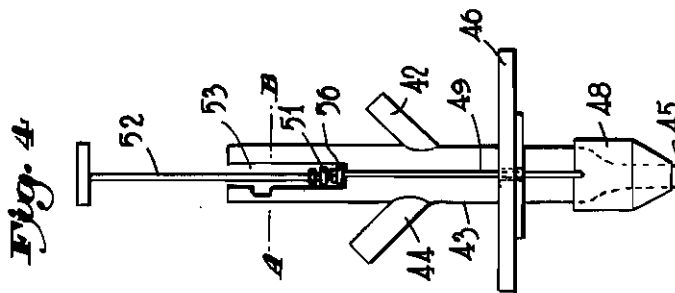
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ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE DECOMPOSITION OF METAL SALTS TO FORM OXIDES

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Application filed February 20, 1941

The present invention relates to an improved process for the thermal decomposition of metal salts, more particularly sulphates, and chlorides or the like, which tend to fuse before complete decomposition is obtained, in order to form metal oxides and gaseous substances which contain the salt forming acid residue in a decomposed or undecomposed form.

The present application is a continuation-in-part of my application Serial No. 208,700, filed May 18, 1938.

One object of the invention is to improve the uniformity and completeness of the decomposition and to reduce the consumption of heat by the decomposition process.

Another object of the invention is to produce the metal salts in the form of a powder having special properties which render them particularly suitable for the thermal decomposition and, in particular, to permit working at a lower decomposition temperature, and atomizing the powders into a gaseous fuel for the purpose of performing the thermal decomposition.

A further object of the invention is to perform the thermal decomposition at the lowest possible temperatures by employing a hot gas containing combustible substances as a heating agent.

Still a further object of the invention is also to produce, at first, a saline powder which is anhydrous or substantially anhydrous and of the most uniform and voluminous nature possible, by the atomization of mixtures of the salts with water or other liquids, such as salt solutions, hydrous melts, and the like, and calcination of the atomized material by means of a gaseous drying agent. This powder is ground, then atomized in a decomposition chamber, and passed in concurrent flow with a hot gaseous agent through the preferably tower-shaped decomposition chamber. The oxides resulting from the decomposition and, if desired, also the remaining decomposition products are then separated from the heating agent.

Still a further object of the invention is to conduct the atomization and calcination of the mixture of salt and liquid, for example the salt solution or salt melt, in such a way that the calcined salt is produced in the form of very small porous, hollow pellets, as the latter can very easily be crushed or ground into fine powders, and the fine powders produced in this manner are particularly suitable for the subsequent thermal decomposition.

Finally, it is an object of the invention to render the atomization during the calcination

and thermal decomposition very uniform and intense with the aid of suitable atomization devices, so that products of drying and atomization of particularly good quality are obtained.

Further features of the invention will become apparent from the following description thereof.

The thermal decomposition of salts which, like the sulphates of magnesium, iron, zinc, copper and other light and heavy metals, or the chlorides of such metals, decompose at high temperatures with the formation of metal oxides, has been carried out by introducing finely divided mixtures of the salts with liquid substances, for example solutions, hydrous melts or suspensions of the salts, into a decomposition chamber, as shown in application Serial No. 95,304. For introducing the finely divided mixtures of the salts and liquid substances into the decomposition chamber, nozzles have been employed which are also supplied with air, steam or other gaseous media to aid in atomizing the mixtures. The finely atomized mixture of salt and water which passes through the nozzles into the decomposition chamber, on issuing from the nozzles, mixes with a highly heated gaseous decomposition agent with which it flows concurrently through an elongated and preferably tower-shaped decomposition chamber. Through the atomization and the instantaneous vaporization of the water, which occur on intimate mixture of the atomized material with the highly heated heating agent, a very fine distribution of the salts ensues, and in this manner it is possible to perform the thermal decomposition practically completely in the short space of time available. The water content of the salt introduced into the decomposition chamber and the violent evaporation of the water play a decisive part in this operation. However, the evaporation at high temperature of the water introduced with the salt into the decomposition chamber requires a considerable additional expenditure of heat.

Known processes for grinding into powders the salts produced by evaporating or cooling solutions of metal salts and for atomizing the powders, in similar fashion as in the method of application Serial No. 95,304, and treating them with a gaseous heating agent for the purpose of thermal decomposition, have the advantage, it is true, in that no heat must be expended during the thermal decomposition for the evaporation of a solvent, but it has been found that the thermal decomposition was incomplete, even when it was carried out at very high temperatures.

Salts which tend to fuse before complete decomposition takes place possess the decided dis-

advantage that they tend to agglomerate during the decomposition, which agglomeration not only prevents a rapid and complete decomposition of such salts but also tends to cause rapid clogging of the apparatus unless special measures are to be employed. In view of this, salts of this nature, such as iron sulfate, have been very difficult to decompose upon a commercial scale to produce substantially pure decomposition products which are not admixed with a substantial amount of undecomposed salt. While some processes have been developed which, for example, will produce iron oxide of about 90% purity from iron sulfate, such processes require a substantially long period for the decomposition.

The present invention renders it possible to overcome these disadvantages in the thermal decomposition of metal salt powders which tend to fuse before they decompose completely, and is applicable particularly to sulfates and chlorides which are converted into metal oxides or metals at a high temperature, splitting off substances which are gaseous at this temperature. In accordance with the invention, a mixture which may contain a liquid substance and one or more metal salts, for example a solution or a hydrous melt, is first treated in a calcining or drying tower. The treatment in the drying or calcining tower is carried out by introducing the solution, melt, or like mixture of salt and liquid, into the tower in finely atomized form.

The atomization is preferably accomplished with the aid of nozzles wherein a gaseous medium, such as steam or compressed air, is simultaneously employed to accelerate the rate of passage and to improve the degree of atomization of the substances to be atomized through the nozzles. A hot gaseous drying agent is passed through the drying or calcining tower, preferably countercurrently with the atomized material. The calcination or drying is thus preferably carried out in accordance with the process of application Serial No. 88,256. The atomized mixture of salt and water or like liquid may, however, also be passed through the drying or calcining tower concurrently with the heating medium. By both methods the salt is converted into a very fine powder with a low specific gravity in the poured form, of about 0.1 to 0.3, while the counterflow treatment affords the advantage that in most cases the powder is produced in the form of small, hollow pellets. This powder is ground fine or crushed if necessary and atomized into an elongated, preferably tower-like decomposition chamber. A highly heated gaseous heating agent is also introduced into the decomposition chamber in such a way that intimate mixing of the heating agent with the atomized powder ensues. Powder and heating agents are passed in the same direction through the decomposition chamber, and the heating agent is passed therethrough at such a rate that it carries substantially all of the powder along with it out of the decomposition chamber. The powder is then conveniently separated from the heating agent outside the decomposition.

On the way through the decomposition chamber the thermal decomposition of the metal salt powder takes place, and it has been ascertained that in the process of the invention the thermal decomposition proceeds very completely. This is due, in particular, to the fact that the preceding atomization, drying and comminution produce a powder which is prepared in a particularly favorable manner for the subsequent thermal de-

composition. The powder consists of small porous particles so that every single particle of powder can be completely penetrated by the gaseous heating agent. The consequence of this is that the heat of the heating agent is able to make its way unhindered to the core of each small grain of powder, and that, on the other hand, the gaseous substances forming during the thermal decomposition can also escape with constant rapidity from the core of each particle, so that conditions essential to complete accomplishment of the reaction are created. The thermal decomposition takes place best if the atomized mixture is passed in counterflow to the drying agent during the production of the powder from the mixture of metal salt and liquid, since the hollow pellets produced in most cases in this method of producing the powder can be particularly readily and finely comminuted and possess the maximum porosity. This great porosity is of particular importance to the complete accomplishment of the decomposition reaction in view of the short time during which the powder remains in contact with the heating agent in the decomposition chamber. Furthermore, this porosity is of great importance in that the suspension of the powder in the heating gases is facilitated and rendered more uniform.

The uniformity and completeness of the decomposition attained in accordance with the present invention is highly unexpected in view of the nature of the salts treated. For example, in the decomposition of iron sulfate, iron oxide is obtained in which no sulfate content may be ascertained, the resultant oxide being completely free of sulfur. It was to be expected in view of the tendency of the salt powders to fuse during decomposition that agglomeration thereof would result and that the decomposition would therefore be incomplete. It was found, however, that no such agglomeration takes place in the process in accordance with the present invention and that substantially complete decomposition of the metal salt powder takes place during the five to six seconds that it takes for the material to pass through the decomposition chamber in conjunction with the heating gases.

By comparison with methods in which the thermal decomposition is effected by the atomization of solutions, hydrous melts or the like, into the decomposition chamber, the invention not only affords the advantage that no evaporation of water or only substantially less evaporation of water is required during the decomposition, and that correspondingly smaller amounts of heating agent are sufficient, but, in addition, the gases flowing out of the decomposition chamber contain the acid formers evolved, for example sulphur dioxide, sulphur trioxide or hydrochloric acid, in substantially stronger concentration. The recovery of these substances, for example in the form of sulphuric acid or hydrochloric acid, thus becomes substantially more economical. The separation of the solid substances produced from the gases and the plant required therefor also cause less expense, and the decomposition can be carried out, in the range of high temperatures, also in a reducing atmosphere by producing the reducing heating agents required for that purpose by incomplete combustion of fuels. Since, in accordance with the invention, the evaporation of water can be completely or substantially avoided during the thermal decomposition, the heat required for that purpose in the known processes can be employed by rendering the com-

buition correspondingly more incomplete when producing the heating medium and the latter correspondingly more intense in reducing action.

The gases which issue from the decomposition chamber may be passed through heat exchangers after separation of the solid substances produced in accordance with the invention to recover the greater part of their sensible heat. They may, for example, be utilized for the preheating of air which then acts, in part, as air of combustion for the production of the heating medium utilized for the thermal decomposition and, in part, is employed in the production of the salt powder from the mixture of salt and water in the calcining or drying tower. The air is employed, for example, directly as a heating medium in the calcining or drying tower or as air of combustion for the production of the heating medium.

In many cases, for example when sulphates are thermally decomposed to form metal oxides by the process of the present invention, it has been found convenient to employ a gaseous heating medium containing a low content of reducing constituents, for example corresponding to about 2% to 7% of carbon monoxide, to effect the thermal decomposition. For example, producer gas, coke-oven gas or the like is added to the heating medium, or the latter is produced from gaseous, liquid or solid fuels by incomplete combustion. The presence of reducing gases in the heating medium enables the decomposition temperature to be reduced considerably. Thus, for example, in the thermal decomposition of magnesium sulphate, decomposition temperatures of about 1190° C. to 1300° C. are sufficient when atomized salt powder, produced in accordance with the invention, and a reducing heating medium are passed in the same direction, whereas the temperatures must be kept about 200° C. to 300 C. higher if an inert or oxidizing heating medium is employed. In the thermal decomposition of sulphates, in accordance with the present invention, the proportion of reducing constituents contained in the heating medium may naturally not be increased so much that reduction of substantial amounts of the sulphur dioxide or sulphur trioxide produced in the decomposition to sulphur or hydrogen sulphide takes place, since the reduction would substantially increase the heat consumption of the thermal decomposition and, furthermore, the thermal decomposition would become incomplete as other chemical reactions would then play a decisive part.

The thermal decomposition may also be carried out by adding further heat to the mixture of powder and heating medium while it is flowing through the elongated decomposition chamber at least at one point of that chamber for instance by means of burners or heating gas inlets distributed over the length and, also, preferably around the periphery of the decomposition chamber. If the heating medium of a fuel contains combustible substances, such as is the case if it is prepared by the incomplete combustion of a fuel, it is also possible to effect a supplementary heating of the heating medium on its path through the decomposition chamber by the combustion of its combustible constituents. For this purpose extra air may be admitted at one or more points distributed over the length of the decomposition chamber in an amount necessary for the complete or partial combustion of the combustible constituents. The content of reducing constituents in the heating medium is thus greatest, in this embodiment of the process, in the por-

tion of the decomposition chamber in which the heating medium and the salt powder to be decomposed are admitted. This provides the advantage that the thermal decomposition is initiated particularly vigorously in this portion of the decomposition chamber.

The properties of the metal salt powder which are of decisive importance to the subsequent thermal decomposition may further be improved, according to the invention, by employing special nozzles for the atomization of the metal salt solution, hydrous melts or the like. Best results have been obtained with an atomizing device which consists essentially of an inner nozzle, through which a gaseous propelling medium issues. The mouth of the inner nozzle is surrounded by the liquid to be atomized. For example, the inner nozzle is located concentrically within a pipe through which the liquid to be atomized is admitted. A second nozzle which widens towards the outlet end (Delaval) is disposed in front of the inner nozzle. A certain distance is left between the mouth of the inner nozzle and the inlet aperture of the second nozzle and, in accordance with the invention, the arrangement is such that the tangents on the inner wall of the second nozzle determine the cross-sectional aperture of the inner nozzle, i. e. if the lines bounding the inner walls of the second nozzle in the latter's axial longitudinal section are extended towards the inner nozzle, the width of the outlet aperture of this nozzle is equal to the distance between the points of intersection of the two extension lines with the line perpendicular to the axis of the inner nozzle, which goes through the outlet cross-section of this nozzle.

For a more clear understanding of the invention reference is made to the accompanying drawings, which illustrate diagrammatically and by way of example some embodiments of apparatus suitable for carrying out the process in accordance with the present invention, and in which:

Fig. 1 shows a vertical section of one embodiment;

Figs. 2 to 6 relate to the atomization device for the drying tower, Figs. 2 and 3 showing two longitudinal sections through an embodiment of the atomization device, the sectional planes of which are at right angles to one another;

Fig. 4 is a view of the same nozzle;

Fig. 5 is a section along the line A—B in Fig. 4; and

Fig. 6 shows a longitudinal section of the bottom portion of this atomization device on an enlarged scale.

In Fig. 1, 1 is the drying tower, 2 the inlet for the liquid to be atomized, 3 the atomization device. The numeral 4 represents the distributing members for the drying agent which is produced, for example, by the combustion of a gas, such as producer gas, in the combustion chamber 37. The combustion chamber 37 is supplied with a mixture of gas and air through the air inlet 35 and the gas inlet 36. The conduit 38 serves to introduce the combustion gases obtained in the combustion chamber 37 into the distributing members 4 in the drying tower 1. The discharge device 5 is mounted in the base of the tower. It is driven in a known manner by means of a gear wheel 6 and bevel wheel 7 and delivers the metal salt powder into the worm of other conveyor device 8, which may also be equipped as a cooling device. The exhaust gas line 9 of the drying tower is provided with a dust removing device 10 from which the gases are passed into the atmos-

phre or to a second dust removing plant by blower 11 and pipes 12 and 13. The material separated by the dust removing plant passes into the bottom part of the drying tower 1 through the pipe 14. The worm 8 discharges into a mill 15. The calcined material is ground in mill 15 to such an extent that it can easily be entrained by gases. It passes from the mill through a worm 16 into a dosing or apportioning device, by which it is introduced into a current of gas. Said current of gas conveys it into the decomposition tower 22. Air of combustion, combustible gases or other gaseous media may be employed as conveyor gas. For example, the conveyor gas is under suction from the blower 18 and is forced thereby through the apportioning device in which it takes up the metal salt powder. The mixture of conveyor gas and salt powder passes through the pipe 17 either into atomization device 28, which is disposed at the bottom of the decomposition chamber 22 and which is connected by pipe 27 to pipe 17, or it is atomized into the combustion chamber 21 by means of the pipe 29 and the device 39. The mixture of metal salt and conveyor gas may also be introduced at both points of the decomposition chamber. It is likewise possible to provide the inlet for this mixture at the top of the tower.

It is also possible for the blower 18 to convey the combustible gas, which is admitted into the decomposition tower at 28 and 39, and burnt therein in order to produce the heating medium. The air of combustion is then supplied by forcing air by means of blower 19 through the heat exchanger 25 into the pipe 20, from which the air is supplied through the pipes 30, 31, 32, 33, and 34 to various points in the decomposition chamber as air of combustion. Some of the lines 30, 31, 32, 33, 34 may naturally be shut off or be dispensed with, depending on requirements. The blower 19 in this arrangement can also deliver the air of combustion which is needed in the combustion chamber 37. However, it is also possible to deliver the air of combustion for this combustion chamber from separate means. Conversely, the blower 19 may be employed for the delivery of the combustion gas and the blower 18 for the delivery of the air of combustion, in which case, if desired, corresponding alterations are provided for in the connection of the supply pipes to the decomposition chamber. Whereas, in the embodiment described above, the metal salt powder to be decomposed is admitted into the combustion chamber through the burners 28 and/or 39, so that it passes in finely distributed form, together with the heating flames which are generated, into the decomposition chamber, it is possible, in another embodiment of the process, to introduce the metal salt powder into the decomposition chamber separately from the mixture of fuel and combustion air from which the heating flames are produced. The introduction takes place, however, near the heating flames in this case also in such a way that the metal salt powder mixes as quickly and intimately as possible with the heating gases.

The decomposition of the metal salt powder takes place from the point of introduction on the path through the decomposition chamber on which the powder carried by the heating gases travels. The mixture of heating gases and products produced in accordance with the invention flows through the pipe 23 into a dust removing device, for example a cyclone 24. In the latter the bulk of the solid products is separated and

said products are withdrawn from the cyclone through the pipe 62, for example to a cooling device or the like. From the cyclone the gases are passed on through the pipe 63 into the heat exchanger 25, where they give up a large part of their heat. They leave the heat exchanger at temperatures at which the separation of the dust still contained in the gases, for example in the electrical gas purifying plant 26, presents no further difficulties. The practically dust-free gases pass through the pipe 60 into the atmosphere or into a plant 61 for the utilization of the gaseous decomposition products contained in the gases.

The atomization device 3 of the drying tower 1 possesses an inner concentric nozzle 41 (Fig. 2), to which the gaseous propelling medium flows through conduit 42. The liquid to be atomized is supplied through the conduit 44 to the outer nozzle pipe 43 to which the second nozzle 45 is connected. The bottom portion of the atomization device passes through the roof 40 of the drying tower.

The propelling medium is to pass out at speeds which correspond to the velocity of sound, or are below the latter, from the nozzle 41. This requirement determines the shape of this nozzle. The latter develops a divergent gas jet which, directly on passing out of the nozzle, is bounded only by the liquid to be atomized. After a part of its travel it passes into the nozzle 45, issuing from the latter at a correspondingly increased velocity. The nozzle 45 is designed as a Laval nozzle, for example. The uniform jet formation is rendered possible by the fact that the nozzle 45 widens conically towards its mouth and that the imaginary, upward extension of the truncated cone enclosed by the inner walls of the nozzle 45, and represented in Fig. 6 by the lines 57 and 58, exactly fills the mouth of the nozzle 41, that is at that point the cone has the same cross-section, represented by the line 59, as the nozzle mouth 41. Preferably the medium to be atomized arrives in front of the mouth of the nozzle 41 with a certain previous acceleration, which may lie, for example, between about 10 and 30 metres per second. To achieve this acceleration the bottom part of the pipe 43 is tapered by the projection 47 of the nozzle 45 in such a manner that, on flowing through this part, the velocity of the medium to be atomized increases to the extent mentioned. It is then seized by the propelling medium jet issuing from the nozzle 41 and mixes therewith in such a way that the desired fine and uniform distribution is achieved.

The jet of mixture of propelling medium and medium to be atomized, issuing from the nozzle 45, retains the shape imparted to it by the shape of the nozzle for a large section of its travel. A pointed atomization cone and particularly fine atomization are obtained. The mixing of the atomized material with the heating agent also takes place very quickly and uniformly. Steam of any desired tension, for example back-pressure steam, may advantageously be employed as propelling medium for the atomization of hot liquid. When working at temperatures lying substantially below the saturated vapor temperature of the water vapor procurable, other propelling media which may also be employed at elevated temperature are preferably employed.

As the jet issues from the nozzle 45 at high speed, said nozzle is kept free from deposits even under difficult conditions, for example in the atomization of hot concentrated salt solution into

a highly heated heating medium. The formation of deposits is scarcely ever to be feared in practice even on the outer wall of the nozzle 45. However, in order to obtain complete security in this respect, particularly under difficult conditions, the cap 48 which surrounds the bottom part of the pipe 43 and the nozzle 45 (preferably of cylindrical shape externally) is mounted to slide in the longitudinal direction. This cap is secured on two rods 49, for example. The rods 49 are detachably joined at their other end to a bridge 51 by means of screws 50. A handle 52 is rotatably secured to said bridge. The handle passes through the bridge and carries the stop 55 therebelow. The bridge 51 is adapted to slide in the slit 53 in the top part of the pipe 43, said top part of the pipe being closed by base 54 to prevent entry of the medium to be atomized. By means of the stop 55, the bridge 51, together with the rods 49 joined thereto and the cap 48, can be secured in side slots 55 in the pipe 43. When it is desired to operate the cap 48, the stop 55 is turned out of its position of rest in the slots 55 until it lies in the slots 53, and the cap 48 can then be pushed up and down by means of the handle 52. By this movement it is possible to remove any deposits of salt with ease, if such should have formed on the outer nozzle wall. The cap 40 also serves as a heat insulator for the bottom end of the pipe 43 and the nozzle 45.

With this device it is possible to conduct the atomization of the metal salt solution or the like in such a way that, with the aid of counterflow calcination, a uniform powder in the form of extremely porous, small, hollow pellets is produced in the tower 1.

Example

A solution of magnesium sulphate, containing 600 grams of magnesium sulphate per litre, was supplied through the pipe 2 to the atomization device 3 at a temperature of 120° C. Steam at a pressure of from 2½ to 3 atmospheres was employed for the atomization. Combustion gases introduced at a temperature of 1000° C. through the apertures 4 at the bottom of the drying tower 1 were used as heating media. The gases, which left the drying tower at a temperature of 350° C., were freed from salt dust entrained by them in the cyclone 10 and passed through the pipe 13 into the atmosphere. The dust from the cyclone passed through the pipe 14 into the bottom of the drying tower to unite there with the salt dust being deposited in said tower. The salt that was discharged from the drying tower had a water content of 2% to 3%. It consisted mainly of fine porous, hollow pellets in grain sizes below 1 mm., and the hollow pellets were crushed to a fine powder in the mill 15. The powder was admitted by means of a current of producer gas into the decomposition chamber 22 through the pipe 17, 27. The heating gases, which were supplied by the burners 21 and 20, had a temperature of 1400° C. Gas produced in known manner from pit coal in gas producers was burnt. On issuing from the tower 22 the gas had a temperature of 1000° C., and still contained 1% of unburnt components. The magnesium oxide, which mostly accumulated in the cyclone 24, was substantially completely decomposed. Its sulphate content was only from 1% to 2%.

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