

June 2, 1953

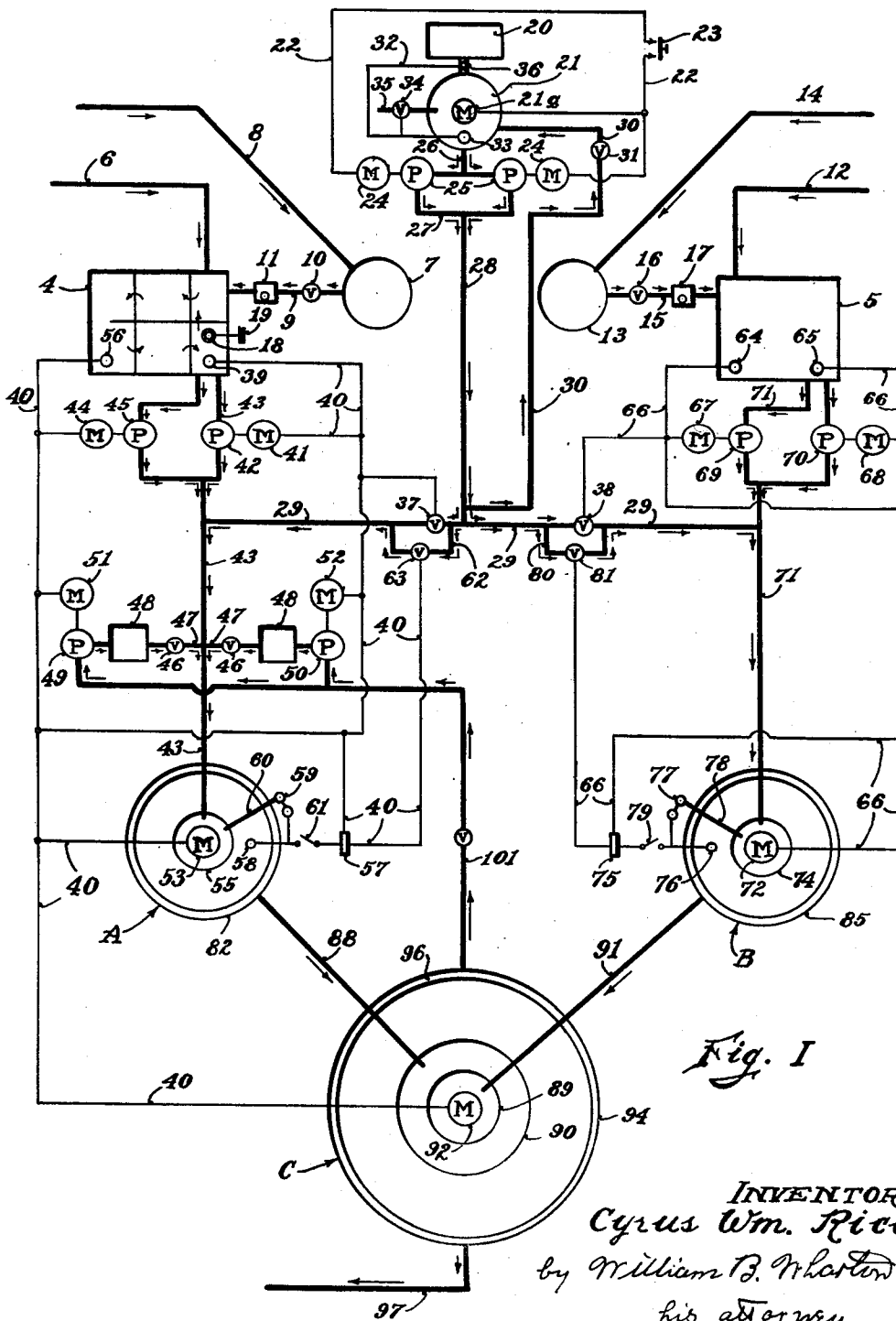
C. W. RICE

2,640,807

METHOD OF WASTE DISPOSAL

Filed March 10, 1949

4 Sheets-Sheet 1



June 2, 1953

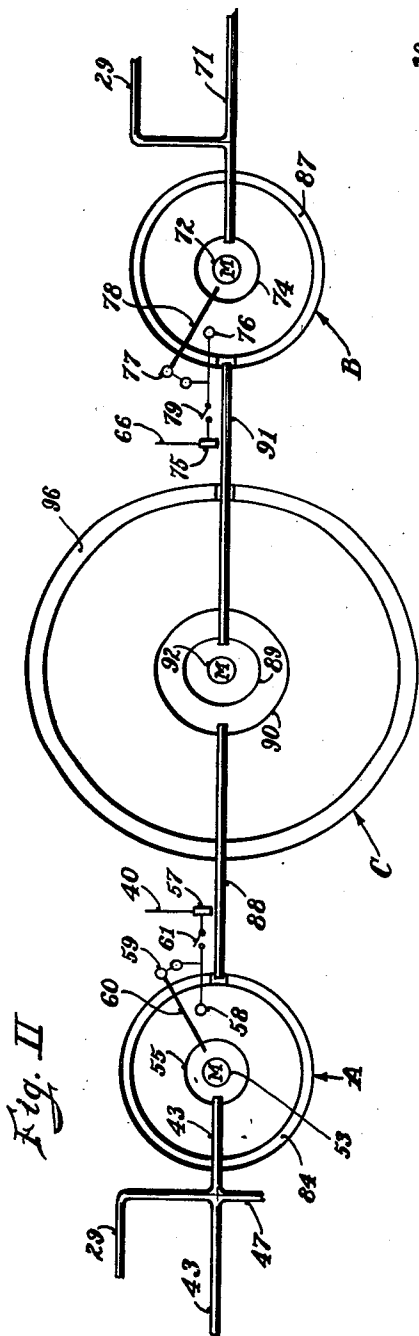
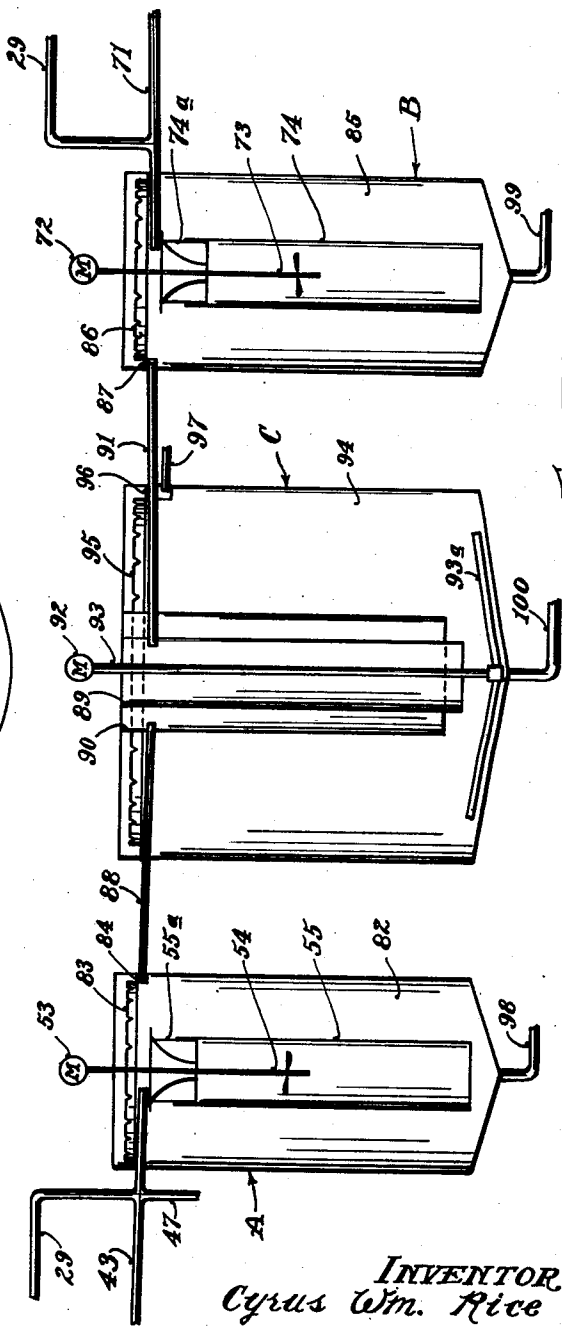
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METHOD OF WASTE DISPOSAL

Filed March 10, 1949

4 Sheets-Sheet 2



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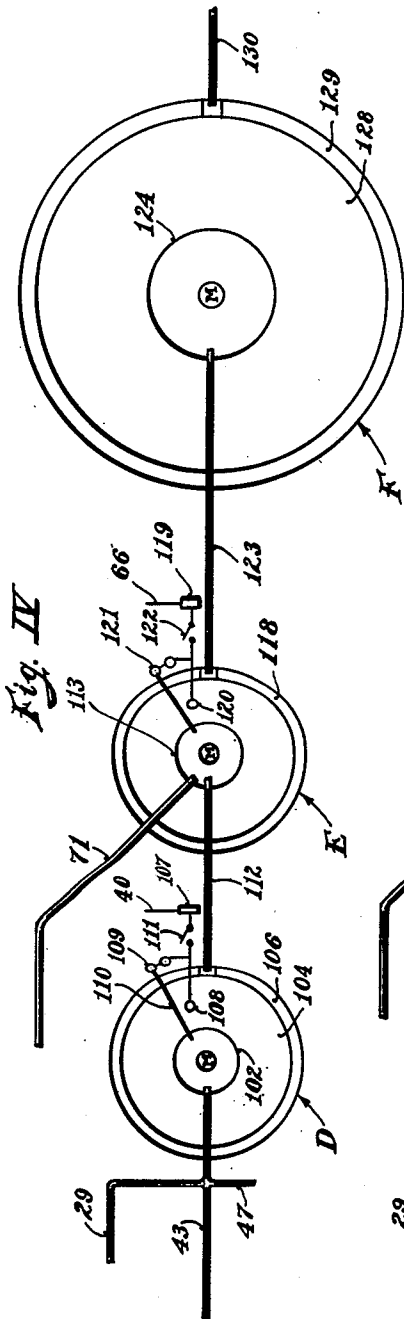
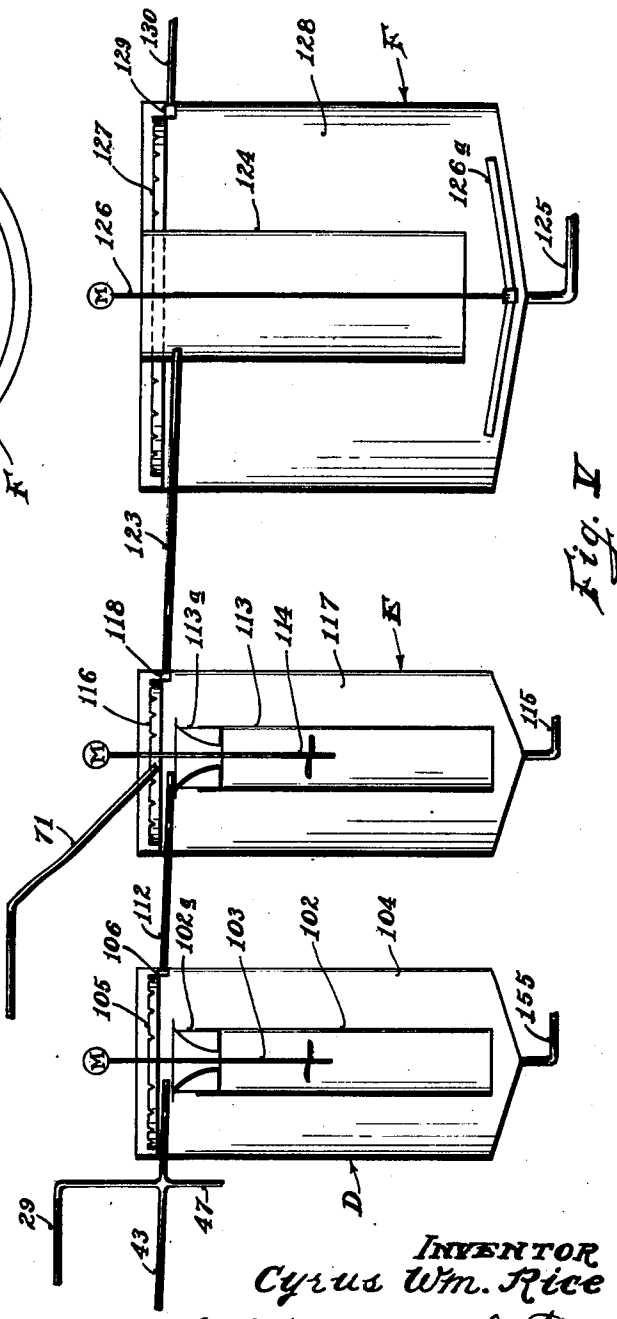
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4 Sheets-Sheet 3



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METHOD OF WASTE DISPOSAL

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4 Sheets-Sheet 4

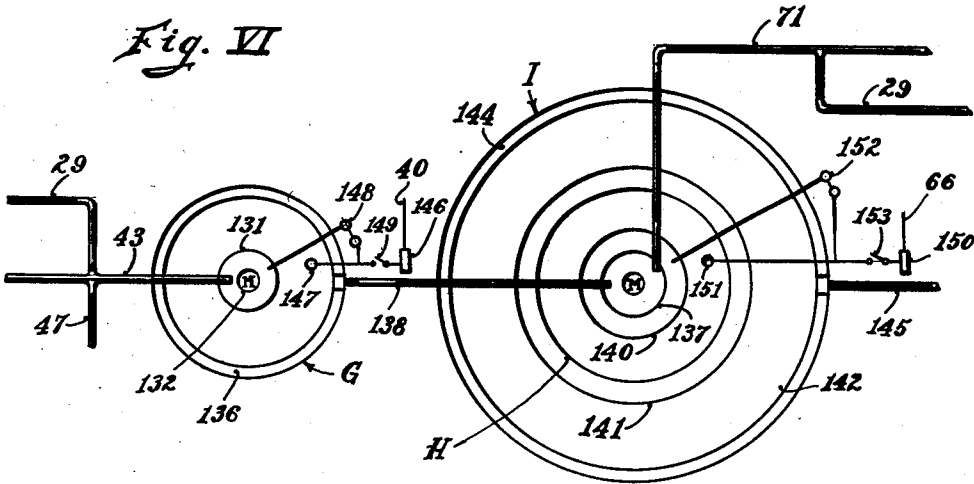
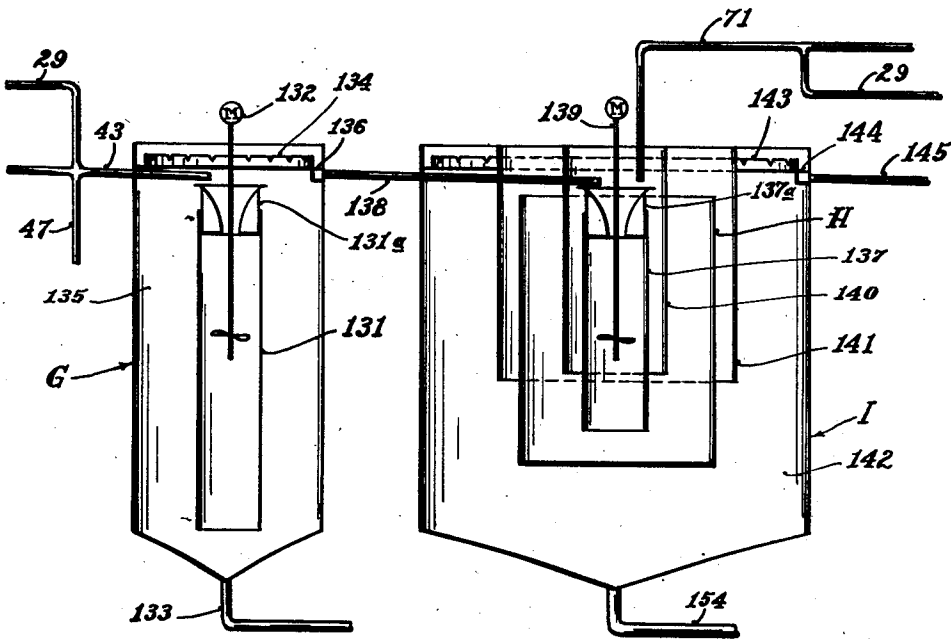


Fig. VII

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UNITED STATES PATENT OFFICE

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METHOD OF WASTE DISPOSAL

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4 Claims. (Cl. 210—2)

1

This invention relates to the treatment of acid and cyanide industrial wastes.

Acid and cyanide wastes are formed adjacently in various industrial operations. For example, in the steel industry pickling operations and cyaniding operations are sequentially performed on bodies of metal for plating with nickel, chrome or the application of other protective or ornamental coatings. Wastes containing sulphuric acid or one of the other mineral acids are highly detrimental if present in streams in substantial concentration and wastes containing cyanides are poisonous to stream life and dangerous to human life if carried into streams in any appreciable quantity. Certainty in operations for disposing of those wastes is therefore a matter of necessity. Certainty in neutralizing the acid wastes and in combining or decomposing the cyanide wastes having been assured, efficiency and economy in the methods of disposal are greatly to be desired. Assuming that the reagents as for neutralization and decomposition must be present in quantity in excess of that theoretically required for those reactions, it is desirable to utilize the reagents in as slight excess as gives certainty in disposal. Also it is desirable, still within the bounds of safety, to minimize the number of tanks required for treating the wastes and for settling the products of the treatment.

One object of my invention is to insure complete neutralization of the acid waste and to insure complete decomposition of the cyanide waste.

Another object of my invention is to provide a system so safeguarded that it is made certain a safe excess of the reagents for rendering the wastes harmless will at all times be supplied, and to minimize the quantity of reagents required for positive safety.

Another object of my invention is to provide simplified plant structure of such sort that it reduces the initial cost of plant installation, while also attaining the other objects of my invention relating to the maintenance of assuredly safe conditions with a minimum expenditure of reagents.

Another object of my invention is to provide a system for disposing of industrial wastes of the type indicated above which is under automatic and correlated control of both the intake of wastes to the system and the supply of requisite reagents thereto to maintain safe conditions, and automatically to safeguard the supply of reagents.

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It may be stated generally that in attaining the objects of my invention, one course I pursue is to maintain a large body of sludge in the conditioning tank for treating the acid waste and in the conditioning tank for treating the cyanide waste. Also I maintain a large body of sludge in a settling tank which is common to both industrial wastes. The conditioning tanks are so arranged that effluent cannot pass from a tank without passing through the body of sludge. In accordance with my preferred procedure, I greatly overtrear the cyanide waste in the cyanide conditioning tank to give an effluent which contains a relatively high alkalinity. I pass this effluent from the cyanide conditioning tank into the acid conditioning tank and then pass effluent from the acid conditioning tank into the common settling tank. In passage through each of these conditioning tanks, the liquid wastes pass through a large body of sludge and carry some of the sludge to the settling tank.

In the accompanying drawings illustrative of installation suitable for the practice of my invention:

Fig. I is a diagrammatic flow plan of a complete installation for conducting my method of waste disposal, including electrical means for controlling the sequential steps of the process.

Fig. II is a diagrammatic plan view showing a group of treating tanks arranged as in Fig. I on an enlarged scale.

Fig. III is a diagrammatic primarily vertical sectional view of the arrangement of treating tanks shown in Fig. II.

Fig. IV is a diagrammatic plan view showing one modification in the arrangement of treating tanks.

Fig. V is a diagrammatic primarily vertical sectional view of the arrangement of treating tanks shown in Fig. IV.

Fig. VI is a diagrammatic plan view showing another modification in the arrangement of treating tanks.

Fig. VII is a diagrammatic primarily vertical sectional view of the arrangement of treating tanks shown in Fig. VI.

Referring initially to Figs. I, II and III of the drawings, reference letter A designates a treating tank for cyanide waste, reference letter B designates a treating tank for acid waste and reference letter C designates a common settling tank for both the treated cyanide waste and the treated acid waste. Associated with these several treating tanks there is a cyanide collection tank 4 and an acid collection tank 5. It will be

assumed that the cyanide is one commonly used in the plating of metal surfaces, such as the highly poisonous sodium or potassium cyanides. It also will be assumed that the acid is one of the corrosive mineral acids used in pickling operations on metals, of which acids sulphuric acid may be taken as typical. The end result of the treatment is, as above explained, so to react wastes containing such substances as to render them innocuous.

As above noted the wastes which are subjected to treatment are a cyanide waste and a mineral acid waste. In my process as hereinafter described the more dangerous cyanide waste obtains in addition to its individual treatment the advantage of increased retention as mixed with the more profuse sludge from the treatment of the acid. As described the system comprises individual treating, or conditioning, tanks for each of the two diverse wastes and a settling tank common to both.

It should be understood that the process has greater flexibility than is presented directly in the specific description by which it is illustrated. Thus, the wastes which are treated may be organic as well as inorganic, such for example as acetic acid waste, the wastes from paper-making, tanning and the like which should not be allowed to pass into streams in unaltered condition, but must be brought into a safe condition approved by supervisory bodies. Also the wastes from other than industrial processes can be included properly in the treatment. Thus, for example, sewage and other organic refuse may be treated in accordance with the process.

Also, it is possible to conduct the process while individually treating more than two wastes which receive conditioning reagent from a single source; and it is possible to conduct the process while running more than two wastes into a common settling tank. This primarily involves merely duplication of collection tanks, conditioning tanks and controls and the correlation of those apparatus elements and the wastes subjected to treatment into the general operation of the process.

Also taking the illustrative installation as it stands, it is possible to conduct the process using only one-half of the system up to the settling tank. In so doing there will be full advantage derived from a continuously and instantly available supply of reagent and of the control conditions by which the reagent is supplied as the flow of the waste to treatment begins, and in which the quantity of such reagent is controlled by desired conditions in the conditioning receptacle in which the waste is subjected to treatment. Insofar as sludge accumulation in the settling tank is concerned, in an operation so conducted such sludge will be supplied by the reactions of the particular waste subjected to treatment, but may be supplemented by sludge derived from previous treatment in the other half of the system or by arbitrary addition of sludges.

As the process is hereinafter described, the employed reagents are given as chlorine and calcium hydroxide solution (milk of lime), as reagents typical for decomposition of the cyanide and the mineral acid. Even in the treatment of those particular wastes calcium hydroxide is given as exemplary of a reagent which releases free hydroxyl ions in water solution and which suitably may be used. In treating wastes of other types other reagents may be more desirable.

As commonly resulting from the cyanide treatment of metals, such as iron and steel, there are two forms of cyanide waste. One such form consists of the cyanide liquor which is discharged from time to time from a cyaniding tank. Such waste is highly concentrated. The other form of cyanide waste consists of the rinse water in which metal from the cyaniding tank has been rinsed, this waste being of course relatively dilute. The same is true with respect to the acid waste, the acid rinse water being presented for disposal in relatively great volume and the concentrated acid waste being presented in relatively small volume. In order that the process may proceed accurately it is necessary in both instances that the dilute rinse water and concentrated waste be mixed to give uniformity in the concentration of the wastes which are treated. To mix the total drainage of the vat in which metal is treated with either acid waste or cyanide waste with the rinse water at any one time would require an unduly large pit or collection tank for the mixing.

Collection pit, or tank, 4 for the cyanide waste contains primarily cyanide rinse water which is brought to the tank by line 6. A tank 7 for concentrated cyanide waste receives that waste by way of line 8 and delivers it through line 9 to the collection pit, or tank. This line 9 is controlled by valve 10 which opens under the influence of float box 11. Similarly, a line 12 brings acid rinse water to acid collection tank 5, and that tank also receives concentrated acid waste from a tank 13 which receives that waste by way of a line 14 and passes it to collection tank 5 by way of a line 15. Line 15 is under the control of a valve 16 operated by a float box 17. The concentrated cyanide waste and the concentrated acid waste are bled evenly over the operating period into the cyanide collection tank 4 and acid collection tank 5 under the influence of the respective float boxes 11 and 17, each of which is provided with a filter and a fixed measuring orifice. A circulating agitator 18 operable under the influence of a timer 19 is provided to insure uniformity in the composition of the waste liquor in collection tank 4. It is to be understood that either or both tank 7 for concentrated cyanide waste and tank 13 for concentrated acid waste may be of the portable sort. The manner of proportioning the introduction of concentrated wastes into the dilute wastes with blending avoids the necessity of large capacity tanks in order to insure a waste liquor for treatment which is of uniform concentration and reasonably dilute.

Any of the known reagents suitable for rendering cyanide waste and acid waste innocuous may be used in conducting a treatment in accordance with the method of my invention. Assuming, for example, that the typical reagents chlorine and calcium hydroxide are used, I have found it desirable automatically to prepare a lime solution and to maintain it under such conditions as to render it instantly available.

The organization for supplying lime solution for reaction comprises a storage bin 20 for dry lime, a lime solution tank 21 and an electrical operating circuit 22 having a push button controller 23. When circuit 22 is energized it operates the motors 24 of two cooperative pumps 25 which draw solution from tank 21 by way of line 26 and also energizes motor 21a which actuates an agitator in lime solution tank 21. Both pumps communicate with a line 27 one branch 28 of which leads to a supply line 29 and the

other branch of which is a recirculating line 30 returning lime solution to tank 21 by way of pressure relief valve 31. These pumps operate continuously during the functioning of the system to maintain a constant pressure of the lime solution in lime supply line 29. A second electrical circuit 32 is energized by a float-controlled switch 33 to open solenoid valve 34 and admit water to the tank by way of water line 35. Simultaneously it introduces finely divided solid lime to the tank from bin 20 by the action of an electrically operated measuring feeder 36. This organization automatically insures an adequate supply of lime solution at all times during the functioning of the system, and by keeping that solution continuously under pressure renders it instantly useful.

Assuming that the system is prepared for operation, with a pressure of lime solution built up in lime supply line 29 and exerting pressure on solenoid-controlled valves 37 and 38 positioned respectively in supply line 29 on opposite sides of its connection with line 28 leading from lime solution tank 21, and with cyanide waste and acid waste in tank 4 and 5 respectively, the system is placed automatically in operation when the liquid level in either or both of those tanks rises above a prescribed point.

Referring first to collection tank 4 for cyanide waste, a float-controlled switch 39 acts to energize electrical circuit 40 and thus to initiate a series of operations, when the liquid level reaches the point for which the float is set. Thus, energization of circuit 40 starts motor 41 which actuates pump 42 drawing cyanide waste from tank 4 into cyanide line 43 and energizes motor 44 which actuates cooperative draw-off pump 45. Simultaneously, solenoid valve 37 in lime supply line 29 is opened to permit lime solution to enter cyanide line 43. Also simultaneously, chlorine is pumped into cyanide line 43 past pressure relief valves 46 in lines 47 from chlorine storage tanks 48 by cooperative pumps 49 and 50 actuated respectively by motors 51 and 52, and a motor 53 is energized to operate an agitator 54 (Fig. III) in downcomer 55 of cyanide-conditioning tank A. At the upper end of downcomer 55 there is a vertically adjustable funnel 55a the adjustment of which influences the extent of the aeration to which the waste is subjected in its treatment.

It may be noted that a second float-controlled switch 56 operated by a float placed at a higher level than the float of switch 39 acts to energize the motors of the draw-off pumps and chlorine pumps and to operate solenoid valve 37 in the lime supply line and the agitator of cyanide conditioning tank A. This second switch 56 acts if for any reason switch 39 should fail to operate.

Also operable when the electrical circuit 40 is energized by either float-controlled switch, there is a pH controller 57 communicating electrically with an electrode 58 and filtering sampler 59, which latter communicates with the interior of conditioning tank A by way of a duct 60. A switch 61 provides for disconnection between the pH controller and electrode to provide for changing electrodes. A by-pass connection 62 in lime supply line 29 by-passing solenoid valve 37, contains a solenoid valve 63 to which circuit 40 is completed under the influence of pH controller 57. Valve 37 remains open to supply a predetermined quantity of the lime solution for treating the cyanide waste. Valve 63 opens intermittently to admit additional lime solution to the cyanide

line at such times as the pH value of waste being treated in conditioning tank A falls below a prescribed minimum.

The organization with respect to the withdrawal and treatment of acid waste is identical except that no provision is made for supplying chlorine to the line conducting acid waste for treatment from acid storage tank 5 to acid conditioning tank B. Here also we have a float-controlled switch 64 and a second switch 65 operated by a float set at a higher level, either of which switches acts to energize electrical circuit 66. Energization of circuit 66 starts the same general series of operations as previously described with respect to the cyanide waste, energizing motors 67 and 68 which operate pumps 69 and 70 and drawing off acid waste into acid line 71 leading to acid conditioning tank B. At the same time solenoid valve 38 in lime supply line 29 is opened to admit lime solution to acid line 71. Also motor 72 which operates an agitator 73 (Fig. III) in downcomer 74 of acid conditioning tank B is energized. At the upper end of downcomer 74 there is a vertically adjustable funnel 74a the adjustment of which influences the extent of the aeration to which the waste is subjected to treatment.

Also operable when the electric circuit is energized by either float controlled switch, there is a pH controller 75 communicating electrically with an electrode 76 and filtering sampler 77, which latter communicates with the interior of conditioning tank B by way of a duct 78. A switch 79 provides for disconnection between the pH controller and electrode to provide for changing electrodes. Valve 38 remains open to supply a predetermined quantity of the lime solution for treating the acid waste. A by-pass connection 80 in lime supply line 29 by-passing solenoid valve 38 contains a solenoid valve 81 to which circuit 66 is completed by pH controller 75. Valve 81 thus opens intermittently to admit additional lime solution to acid line 71 at such times as the pH value of waste being treated in conditioning tank B falls below a prescribed minimum.

Cyanide waste entering cyanide conditioning tank A by way of cyanide line 43 enters downcomer 55 of the tank and passes downwardly therethrough, being agitated in passage by agitator 54. It is to be understood that with this cyanide waste there is included lime solution entering line 43 by way of lime supply line 29 and chlorine entering cyanide line 43 by way of chlorine supply line 47. In Figs. II and III the position and arrangement of the lime supply line and the chlorine supply line is simplified to bring those lines into the illustration of those figures of the drawings. In passage of the cyanide waste downwardly in downcomer 55 of the cyanide conditioning tank, the waste is aerated by air induced over the lip of funnel 55a by the action of agitator 54. In the downcomer the reactions which have begun in cyanide line 43 are continued, and upon issuance of the waste undergoing treatment from the lower end of downcomer 55 into the outer chamber 82 of conditioning tank A, it meets and is vigorously mixed with a volume of sludge which is allowed to build up at the base of the tank. As the level of liquid rises in cyanide conditioning tank A because of aeration and incoming waste it passes over a saw-toothed overflow 83 into an annular trough 84 from which it passes as effluent to settling tank C. This effluent waste, which is highly aerated,

carries with it into tank C some of the alkaline sludge with which it is mixed in conditioning tank A.

Acid waste entering acid conditioning tank B by way of acid line 71 enters downcomer 74 of the tank and passes downwardly therethrough, being agitated and aerated in passage by agitator 73. It is to be understood that with this acid waste there is included lime solution entering acid line 71 by way of lime supply line 29. In Figs. II and III the position and arrangement of the lime supply line is simplified to bring that line into the illustration of those figures of the drawings. In passage of the acid waste downwardly in downcomer 74 of the acid conditioning tank, the reactions which have begun in acid line 71 are continued. In the downcomer and upon issuance of the waste undergoing treatment from the lower end of downcomer 74 into the outer chamber 85 of acid conditioning tank B it meets and is vigorously mixed with a volume of sludge which is allowed to build up at the base of the tank. As with the cyanide waste, the acid waste is aerated by air which is induced as liquid flows into the downcomer over the lip of funnel 74a for recirculation. As the level of liquid rises in acid conditioning tank B because of aeration and incoming waste, it passes over a saw-toothed overflow 86 into an annular trough 87 from which this effluent water passes to settling tank C, carrying with it some of the alkaline sludge from tank B.

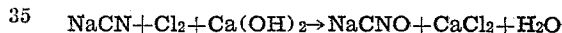
In both conditioning tanks the mixture of waste undergoing treatment and the reagent together with accumulated precipitates is subjected to an aeration which accelerates the treatment. The aeration is effected by induction of air as liquid from the outer chamber of the tank is lifted over the lips of the funnels at the upper ends of the downcomers for recirculation. Thus the level to which a funnel is adjusted controls the volume of recirculated liquid mixture and the air induced by the recirculating inflow. This intimate blending of the wastes and chemical precipitates accompanied by foaming and recirculation assures an effectively complete destruction of the original properties of the wastes. When operating in tanks of a size which may be considered normal for full scale operation, the sludge accumulation in the tanks when quiescent should have a depth of several feet.

Line 88 leading from annular trough 84 of cyanide conditioning tank A enters an annular downcomer provided between the wall of inner downcomer 89 and an outer shell 90 in settling tank C. Passing downwardly through this annular space to its opening in the lower region of tank C, cyanide waste enters a body of sludge carried over from both the cyanide and acid conditioning tanks, or formed by completion of the reactions in the settling tank. Effluent from annular trough 87 of acid conditioning tank B passes by way of line 91 to a space within the inner downcomer 89 of settling tank C and passing downwardly through this downcomer also enters the body of sludge collected in the bottom of the tank. A motor 92 rotates a shaft 93 which carries blades 93a positioned below the lower ends of the downcomers. Such blades are rotated very slowly merely to produce some movement in the sludge toward the center of the tank and thus to facilitate its intermittent withdrawal from the tank. As the level of liquid in outer chamber 94 of settling tank C rises with continued operation of the system, it passes over the saw-toothed overflow 95 into an annular

sump 96 from which it flows as harmless effluent by way of a draw-off line 97.

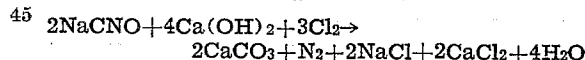
At the base of conditioning tanks A and B and settling tank C there are respectively valved draw-off lines 98, 99 and 100 which may be used to maintain a suitable level of sludge in the several tanks. If the character of the sludge in cyanide conditioning tank A should be questioned, such sludge can be corrected with sludge from acid conditioning tank B before its transfer to settling tank C to become part of the mixed sludge at the base of that tank. Also, if desired, sludge may be transferred from settling tank C to supplement the sludge precipitated in either of the conditioning tanks A and B or sludge from one of those tanks can be transferred to the other of said tanks to supplement the sludge formed therein. In practice the discharged sludge is collected in tank trucks and delivered to a dump.

The reactions involved in rendering the specifically indicated wastes harmless will now be described. As cyanide waste is taken from the cyanide collection tank and flows through the cyanide pump-line to cyanide conditioning tank A, it receives in passage a charge of calcium hydroxide and of chlorine, carrying these reagents with it into the downcomer of the cyanide tank and being thoroughly mixed with the reagents by agitation in the tank. The reactions begin in the cyanide line and continue into the cyanide conditioning tank. As the reactions take place, reaction products are precipitated to form the sludge in the cyanide conditioning tank. These reactions may be illustrated as follows:



This reaction takes place very rapidly and by it the intensely poisonous cyanide is converted to the relatively harmless cyanate.

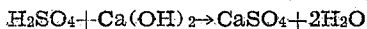
Although these cyanates such as sodium cyanate and potassium cyanate have only about $\frac{1}{1000}$ the toxicity of the corresponding cyanides, the cyanate is itself destroyed by continued reaction with an alkali and chlorine as in accordance with the illustrative formula:



The first reaction given above, which is the reaction primarily effective in destroying the toxic properties of the cyanide waste, is substantially complete within about one or two minutes under conditions of alkalinity exceeding a pH of 8.5. The second reaction takes place within an hour. These are accepted reactions in accordance with literature references. The actual operation of the method as herein disclosed was checked under pilot plant conditions. Under those conditions the results indicated that the first reaction was 95% complete within one minute on waste having an initial 100 p. p. m. cyanide concentration. The second reaction was about 30% complete within two hours and the toxicity of the cyanate being relatively so low the reactions were considered in practical effect completely to have destroyed the toxicity of the cyanide waste. During the test of alkalinity in the cyanide conditioning tank it was maintained at a pH of about 8.7. During the operation of the process as conducted the pH in the cyanide conditioning chamber is therefore to be understood as maintained in excess of a pH of 8.5.

Assurance of adequate treatment of the cyanide waste in its conditioning tank is assured by mixing the reacting waste with a considerable body of the sludge precipitated in the tank.

The treatment of the acid waste is closely similar. Acid waste from the acid collection tank or pump-pit in its passage to acid conditioning tank B receives a charge of lime solution with which it enters the downcomer of the tank and is thoroughly mixed for reaction with the lime solution during passage through the downcomer to the lower region of the tank. The primary reaction is one of the well known neutralizing reactions, such as:



Mixed with the precipitated CaSO_4 there are precipitates of metal hydroxides such as the hydroxides of iron, nickel and chrome going to form the sludge in the lower region of the acid conditioning tank. In this tank the alkalinity is maintained at a pH in excess of 7, such as a pH of 7.5 and higher.

During the operation of the method, flow of lime solution to both the cyanide conditioning tank and the acid conditioning tank is quantitatively under the control of pH controllers 51 and 75 the passage of chlorine to the cyanide conditioning tank being regulated by the setting of valve 46. Whereas the introduction of the lime solution is proportioned according to the pH, the introduction of chlorine is continuous under the action of motors 51 and 52 on pumps 49 and 50 forcing chlorine from tanks 48 past valves 46. The great advantage of placing the flow of lime under the influence of the pH controllers is twofold. From one aspect it assures that there be sufficient alkalinity in the conditioning tanks to carry out the necessary reactions therein. From another viewpoint it assures that the necessary results be obtained with a minimum of the reagents which render the wastes harmless; it being understood that the maintenance of proper alkalinity in the cyanide conditioning tank assures complete utilization of the chlorine which is provided and thus additionally limits the excess of chlorine which it is necessary to provide.

Certainty as to the safety of the operation is also assured by maintenance of very substantial bodies of precipitated sludges in the two conditioning tanks and by the introduction of treated wastes from both tanks into a common settling tank in which a large body of chemical precipitates is maintained. This assures repeated intimate contact of all portions of the wastes with the reagents and renders excess alkalinity in the effluent of the acid conditioning tank effective to insure that the more dangerous cyanide wastes are rendered wholly innocuous. The presence of the substantial bodies of sludges in the two conditioning tanks and in the common settling tank fully protects the system against slugs of wastes having a higher than normal concentration of toxic components. Although the avoidance of slugs is guarded against initially by the blending of concentrated wastes from actual pickling and cleansing operations with the wash waters from those operations, it is possible that there may be some temporary or localized increase in the concentration of the toxic ingredients and against such conditions the passage of wastes undergoing treatment through the sludges gives protection without maintaining an exorbitantly great excess of reagents in the system. Because of the fact that the system is under automatic control the possibility of difficulties rising from human errors and omissions is reduced to a minimum.

A valved return line 401 of trough 96 of the settling tank leads to pumps 49 and 50 which force chlorine from tanks 48 and past valves 46 into cyanide line 43. This backflow of effluent water through the chlorine supply and back to the chlorine line helps to wash chlorine into the treating system and gives the system the full benefit of excess alkalinity in the effluent from the settling tank.

Referring to the modification of the method illustrated by Figs. IV and V of the drawings, it should be understood initially that all the controls as above described with reference to the preceding figures of the drawings are present and function in similar manner. The only modification resides in the arrangement of the two conditioning tanks and the settling tank and the alteration of the sequence of steps so caused. The modified course followed by the wastes in accordance with this variant of the process is illustrated by the arrangement of cyanide conditioning tank D, acid conditioning tank E and settling tank F which correspond in structure though not in arrangement to the analogous tanks A, B, and C as previously described.

Thus as shown in Figs. IV and V cyanide line 43 leads to downcomer 102 in cyanide conditioning tank D, the connection of lime supply line 29 and chlorine supply line 47 to this tank being similar to like connections to cyanide conditioning tank A. Similarly an agitator 103 is mounted in downcomer 102 having a vertically adjustable funnel 102a at its upper end and the downcomer empties adjacent the lower region of the tank into the bottom and outer chamber 104 of the tank. A valved draw-off line 115 for sludge is provided at the base of the tank. Similarly to cyanide conditioning tank A, tank D is equipped with a saw-toothed overflow 105 over which treated water passes into annular trough 106 when the level of liquid rises sufficiently in the tank. Similarly to cyanide conditioning tank A, cyanide conditioning tank D is equipped with a pH controller 107 in electrical control circuit 40. The pH controller communicates electrically with an electrode 108 and filtering sampler 109 which latter communicates with the interior of conditioning tank D by way of a duct 110. A switch 111 provides for a disconnection between the pH controller and the electrode to provide for changing electrodes. Instead of passing directly to a settling tank, however, draw-off line 112 from annular trough 106 of the cyanide conditioning tank empties into downcomer 113 of acid conditioning tank E.

This tank E similarly is equipped with agitator 114 in downcomer 113, vertically adjustable funnel 113a at the upper end of the downcomer, valved draw-off line for sludge 115, a saw-toothed overflow 116 at the upper end of outer chamber 117 of the tank from which the upper level of liquid passes into annular trough 118. It also is similarly equipped with pH controller 119, electrode 120, filtering sampler 121 and disconnecting switch 122. The pH controller is in communication with the general electrical control circuit 66 of the system. Line 71 conducts acid wastes and lime solution to downcomer 113 to meet treated cyanide waste delivered by draw-off line 112 from cyanide conditioning tank D.

From the annular trough 118 of acid conditioning tank E a draw-off line 123 leads to the downcomer 124 of settling tank F. Settling tank F is similar in construction to settling tank C previously described. Like settling tank C it has a valved draw-off connection 125 for excess sludge

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and an agitator 126 which is slowly motor driven to move sludge by means of blades 126a toward the center of the tank at its base. Settling tank E also has in its upper region a saw-toothed overflow 127 over which the upper level of liquid in the outer chamber 128 of the tank flows into annular trough 129. A draw-off line 130 withdraws effluent from trough 129. It is to be understood that a second valved line similar to the valved return line 101 shown in Fig. I can be provided either as independently connected with trough 129 or as a branch of draw-off connection 130 to recirculate effluent through chlorine pumps 49 and 50 and storage tanks 48 into cyanide line 43 leading to cyanide conditioning tank D.

The modification of the method as illustrated by the apparatus arrangement suitable for its practice shown in Figs. IV and V of the drawings is preferred procedure. In conducting this variant of the method the pH controller associated with the cyanide conditioning tank is set to maintain a high excess alkalinity in that tank to the extent of maintaining a pH of 11 or even higher. This places the emphasis of the process on the destruction of the highly toxic cyanide waste which receives initially a very great overtreatment. The excess alkalinity from this overtreatment serves to treat the acid waste in the acid conditioning tank. Because the reactions by which the initial cyanide content of the cyanide waste is destroyed are irreversible this can be done with complete safety insofar as the cyanide waste is concerned. As additional assurance, however, that the wastes of both types will be rendered innocuous the pH controller of acid conditioning tank E maintains in the acid conditioning tank an alkalinity, such as is indicated by a pH in excess of 7.5, adequate to insure complete treatment of the acid waste as well as the cyanide waste. As in the practice previously described this is done by introducing an alkaline reagent such as lime solution into the acid line leading to tank E at such times as the pH in the tank tends to drop.

It will be noted that in this modification of the process, also, wastes of both kinds pass to a common settling tank before being discharged as effluent. Thus in this modification, also, both wastes undergoing treatment are mixed at least twice with bodies of alkaline sludge in the several tanks and the cyanide waste is mixed three times with sludge before being discharged as effluent. As explained above, this repeated mixture with sludge insures against the inclusion of imperfectly treated waste in the ultimate effluent under abnormal conditions in which slugs of increased concentration pass through the system. With respect to the dangerous cyanide wastes this modification also provides a sludge admixture addition to that provided by practice of the method as illustrated in Figs. I to III of the drawings. As in the procedure applicable to Figs. I to III, the use of a settling tank common to the wastes of both kinds insures an adequate volume of sludge in the final tank of the system and gives to the dangerous cyanide waste the advantage of final treatment in a body of sludge to the formation of which the precipitation of products from treatment of the acid waste has contributed.

The method as conducted in accordance with the procedure illustrated in Figs. VI and VII is identical with the method as described in connection with Figs. IV and V of the drawings. The only difference involved in the showing of Figs. VI and VII is in the telescoping of apparatus to simplify the installation in which the method is performed and to economize in the

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plant space required for installation. Here again it is to be understood that all the elements and controls associated with the conditioning and settling tanks as shown in Fig. I of the drawings are present in an installation having the arrangement of conditioning and settling tanks shown in Figs. VI and VII.

Referring to the apparatus as shown in Figs. VI and VII of the drawings, this apparatus comprises a cyanide conditioning tank G, an acid conditioning tank H and a settling tank I, the acid conditioning tank H being arranged within settling tank I. Thus cyanide conditioning tank G comprises a downcomer 131 equipped with a vertically adjustable funnel 131a at its upper end and with a motor driven agitator 132 and a valved draw-off line for sludge 133. Cyanide line 43 in communication with lime supply line 29 and chlorine line 47 opens into the upper end of downcomer 131. Similarly to the analogous tanks which previously have been described cyanide conditioning tank G is shown as provided with a saw-toothed overflow 134 over which liquid rising in the outer chamber 135 of the tank passes into annular trough 136.

The combination of acid conditioning tank H and settling tank I comprises a downcomer 137 having a vertically adjustable funnel at its upper end into which discharges draw-off line 133 for effluent from the cyanide conditioning tank. Acid line 71, to which connection with lime supply line 29 is shown, also discharges into downcomer 137. In downcomer 137 there is a motor-driven agitator 139 and at its lower end the downcomer opens into a downwardly closed receptacle which serves as the acid conditioning tank H. Surrounding downcomer 137 there is a baffle sleeve 140 which extends to the upper end of the tank and surrounding acid conditioning tank H there is a second baffle sleeve 141 which also extends to the upper end of the tank. It will be noted that the upper and receiving end of downcomer 137 lies above the upper end of the acid conditioning tank H and is equipped with vertically adjustable funnel 137a. In the upper region of the settling tank I in the outer chamber 142 thereof and surrounding outer baffle sleeve 141 there is a saw-toothed overflow 143 over which the upper level of liquid in the settling tank can flow into annular trough 144. A draw-off line 145 receives effluent from trough 144 and it will be understood that a return line for conveying effluent to the chlorine pumps desirably also is provided as shown in Fig. I of the drawings and as above discussed. Similarly to the conditioning tanks as previously disclosed a pH controller is associated with cyanide conditioning tank G and with acid conditioning tank H standing within settling tank I. Thus, as shown, cyanide conditioning tank G has associated therewith a pH controller 146 in communication with electrical control circuit 40 and with an electrode 147 and a filtering sampler 148 communicating with the interior of the tank. A switch 149 provides for disconnection between the pH controller and electrode to provide for changing electrodes. Similarly acid conditioning tank H has associated therewith a like organization of pH controller 150 in communication with electrical control circuit 66, an electrode 151, a filtering sampler 152 and switch 153 for changing electrodes.

Cyanide waste entering cyanide conditioning tank G is treated identically as in cyanide conditioning tank D shown in the apparatus organization of Figs. IV and V, excess alkalinity to the extent represented by a pH of 11 or over be-

ing maintained in the tank. Effluent from the cyanide conditioning tank passing into downcomer 137 in the acid conditioning tank and settling tank assembly meets with acid waste and is thoroughly mixed within the acid conditioning tank, the excess alkalinity of the cyanide waste undergoing treatment providing neutralizing reagent for the acid waste. As in acid conditioning tank E of Figs. IV and V, the pH controller of acid conditioning tank H serves to maintain alkalinity at a suitable value in excess of 7.5 in the acid conditioning tank.

As the level of liquid in the downwardly closed acid conditioning tank rises, that liquid flows over the lip of the tank into the annular space between the wall of the tank and outer baffles 141 and downwardly in that space to the bottom and outer chamber of settling tank I. Under the influence of agitator 139 sludge also is carried over the lip of acid conditioning tank H and into the settling tank I. When settling tank I has filled, the liquid which as in other variants of my process consists of clear and harmless water, flows over saw-toothed overflow 143 into annular trough 144 and is discharged as effluent through line 145 or is recirculated back to the chlorine pumps. It should be noted that sludge as well as liquid is carried over the lip of acid conditioning tank H and passes to the bottom of settling tank I. A suitable level of sludge in the settling tank is maintained by drawing-off sludge from time to time by way of valved discharge line 154. It is thus clear that the conduct of the method in the organization of Figs. VI and VII is identical with the method as conducted in the apparatus of Figs. IV and V.

Considering the process purely as a chemical process apart from the disclosed automatic controls, it consists in separately treating two diverse wastes, one of which is more toxic than the other and both of which originate in the form both of concentrated waste and dilute waste. In preparation for reaction these wastes each are blended by a continuous operation, to obtain uniformity of dilution under conditions so controlled that the likelihood of delivery of a waste in its more concentrated form for reaction is minimized. As each of the wastes in its blended form flows to treatment it is charged with a reagent, or reagents, appropriate for reactions which render the waste innocuous. These blended and charged wastes are then treated separately with repeated agitation and aeration in admixture with sludge, which sludge typically is composed of the products of the reaction by which the wastes are decomposed and contains an excess of the decomposing reagent. After reaction with agitation and aeration for a period sufficient under normal circumstances to render the wastes harmless, they both pass as effluent to a common settling receptacle in which the effluents mix with a body of sludge in the settling receptacle and remain for a further retention period under conditions in which there is an excess of the decomposing reagent, until they finally pass as a common and harmless effluent from the settling tank.

As a preferred modification of this process, there being a reagent appropriate to the treatment of both the said wastes, the more toxic of the two wastes is treated with a great excess of the common reagent. The effluent from this waste then carries an excess of that common reagent to a receptacle in which such excess is employed in treating the second waste. In this reaction additional reagent is supplied if necessary in order to assure complete decomposition of

both wastes. The combined effluent then passes from the second receptacle to a settling receptacle for further retention and ultimate discharge.

Considered from the viewpoint of automatic control as well as of purely chemical process, a supply of the reagent which is common to the wastes of both types is maintained under constant pressure for instantaneous addition to the wastes in their passage to treatment. Addition of this common reagent is made automatically and instantaneously under the influence of the electrical controls which initiate flow of the wastes to their individual treatments. In conjunction with the initial blending of each of the wastes with respect to its concentrated and dilute occurrence, this instant supply of reagent prevents the passage of slugs of raw waste to treating receptacles apart from the reagent with which that waste is to be reacted. Further controls automatically supply such quantity of the additional reagent as may be required to maintain conditions appropriate to the complete decomposition of the two wastes in their initial treatment. These controls are such as to maintain excess of reagent in effluent from the initial treatments passing to the common settling container.

It will be understood that it may be desirable even though there be only one particular waste to be subjected to treatment that the supply of such waste be divided for initial treatment, but that the effluents from the initial treatments be brought together for a common settling period before an ultimate effluent is discharged. Also that any number of diverse wastes initially treated may be brought to a common settling tank and maintained under such chemical conditions as give additional assurance as to the harmless nature of the combined effluent. In either case, or if an individual waste is simply to be treated by itself as in one-half of the treating system, the automatic blending is of importance when the waste occurs both in concentrated and dilute form. Also such blending may usefully be practiced on unlike wastes both of which can be completely treated by a common reagent and one of which is of such nature that blending with the other before treatment is advantageous. In any event automatic control by which reagent in sufficient quantity is supplied in accordance with the condition of the waste undergoing treatment is an important feature.

I claim as my invention:

1. The method of treating two waste waters from industrial operations which waters respectively contain in solution diverse toxic substances, the said dissolved substance in one said water exceeding that of the other water in toxicity, the reactions for rendering which toxic substances harmless involving at least one common reagent, by flowing the said solutions from volumes of supply thereof to reaction chambers therefor, throughout the flow of said solutions supplying to each thereof reactive material containing the common reagent capable of rendering the toxic substance of the said solution harmless by reaction therewith, the amount of reaction material added being sufficient to supply a substantial excess of said common reagent to the solution containing the toxic substance of greater toxicity, flowing effluent containing excess of the said common reagent from the reaction chamber for the solution having a toxic content of greater toxicity into the reaction cham-

ber for the solution having the toxic content of lesser toxicity, and following reaction in said last named reaction chamber settling the mixed reacted solutions and the solid products of reaction therein and drawing off effluent therefrom.

2. The method of treating two waste waters from industrial operations which waters respectively contain in solution a mineral acid and a cyanide, the reactions for rendering which toxic substances harmless involving as a common reagent a substance capable of supplying free hydroxyl ions in water solution by flowing the said solutions from volumes of supply thereof to reaction chambers therefor, throughout the flow of said solutions supplying to each thereof reactive material capable of rendering the toxic substance of the said solution harmless by reaction therewith, the said hydroxyl ion supplying substance being added to both said solutions and chlorine being additionally supplied to the said cyanide solution, the said hydroxyl ion supplying substance as a common reagent being added in substantial excess to the solution containing cyanide, flowing effluent containing excess of the said common reagent from the reaction chamber for the cyanide solution into the reaction chamber for the mineral acid solution, and following reaction in said last named reaction chamber settling the mixed reacted solutions and the solid products of reaction therein and drawing off effluent therefrom.

3. The method of treating two waste waters from industrial operations which waters respectively contain in solution diverse toxic substances the said dissolved substance in one said water exceeding that of the other said water in toxicity, the reactions for rendering which toxic substances harmless involving at least one common reagent, at least one of said waste waters occurring in the form of a relatively dilute and a relatively concentrated solution of the toxic substance therein, in the receptacle containing a volume of supply of the said dilute solution automatically flowing off sufficient solution from the volume of supply to a reaction chamber on inflow of the more dilute solution to maintain a constant level of solution in the receptacle containing said volume of supply, continuously making a blend of the said more dilute and concentrated solutions by bleeding the more concentrated solution of the said toxic substance into the more dilute solution thereof during flow from the said volume of supply, flowing the said diverse solutions each to a reaction chamber therefor, throughout the flow of said solutions automatically supplying to each thereof reactive material, containing the common reagent, capable of rendering the toxic substance of the said solution harmless by reaction therewith, the amount of reaction material added being sufficient to supply a substantial excess of said common reagent to the solution containing the toxic substance of greater toxicity, flowing effluent containing excess of the said common reagent from the reaction chamber

for the solution having a toxic content of greater toxicity into the reaction chamber for the solution having the toxic content of lesser toxicity, and following reaction in said last named reaction chamber settling the mixed reacted solutions and the solid products of reaction therein and drawing off effluent therefrom.

4. The method of treating two waste waters from industrial operations which waters respectively contain in solution a mineral acid and a cyanide, the reactions for rendering which toxic substances harmless involving as a common reagent a substance capable of supplying free hydroxyl ions in water solution, at least one of said waste waters occurring in the form of a relatively dilute and a relatively concentrated solution of the toxic substance therein, in the receptacle containing a volume of supply of the said dilute solution automatically flowing off sufficient solution from the volume of supply to a reaction chamber on inflow of the more dilute solution to maintain a constant level of solution in the receptacle containing said volume of supply, continuously making a blend of the said more dilute and more concentrated solutions by blending the more concentrated solution of the said toxic substance into the more dilute solution thereof during flow from the said volume of supply, flowing the said diverse solutions each to a reaction chamber therefor, throughout the flow of said solutions supplying to each thereof reactive substance capable of rendering the toxic substance of the said solution harmless by reaction therewith, the said hydroxyl ion supplying substance being supplied to both said solutions and chlorine is additionally supplied to the said cyanide solution, the said hydroxyl ion supplying substance as a common reagent being added in substantial excess to the solution containing cyanide, flowing effluent containing excess of the said common reagent from the reaction chamber for the cyanide solution into the reaction chamber for the mineral acid solution and following reaction in said last named reaction chamber settling the mixed reacted solutions and the solid products of reaction therein and drawing off effluent therefrom.

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