July 13, 1965 I. R. HIGGINS 3,194,663

RADIOACTIVE DECONTAMINATION OF MILK

Filed April 1, 1963 5 Sheets-Sheet 1

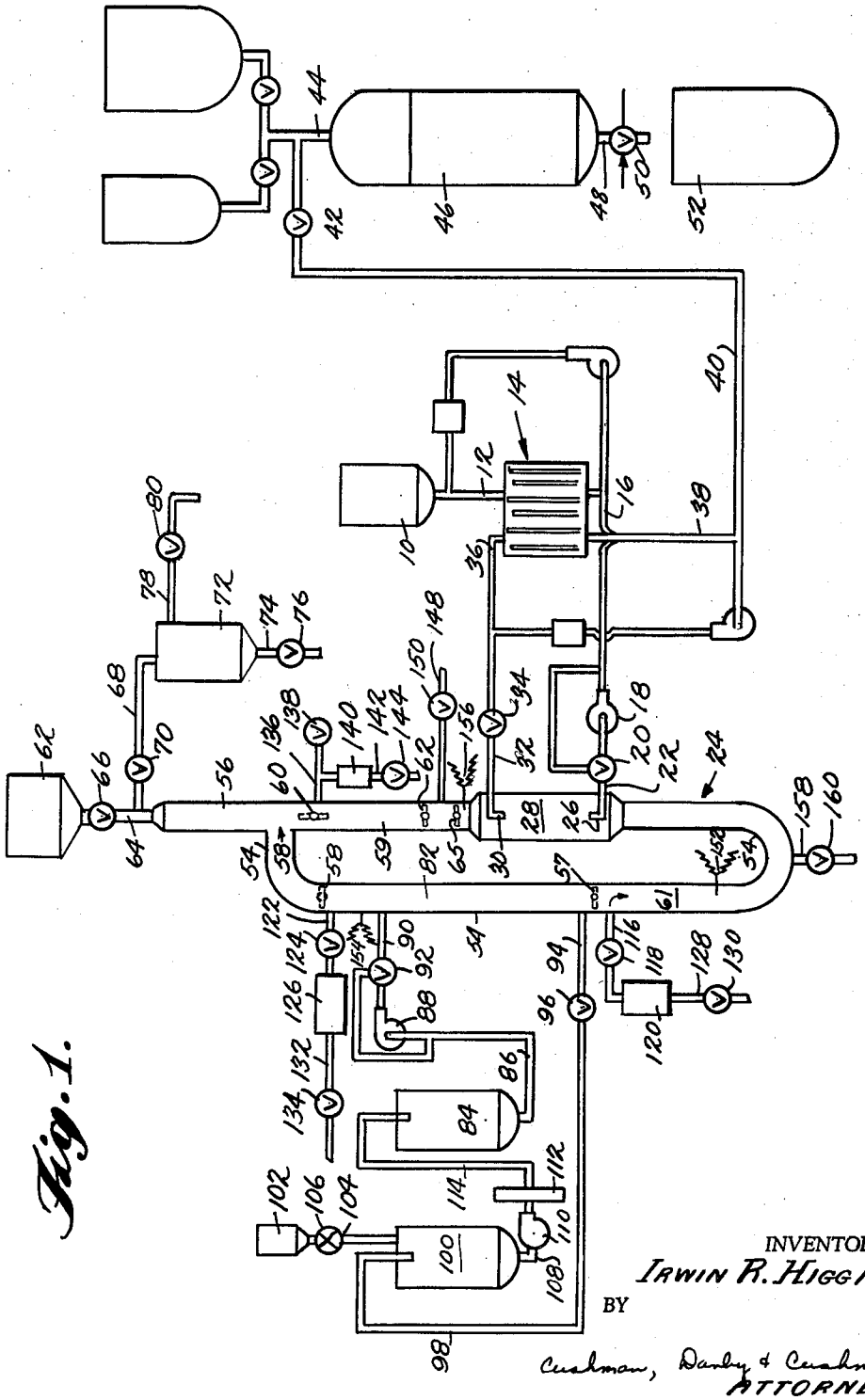


Fig. 1.

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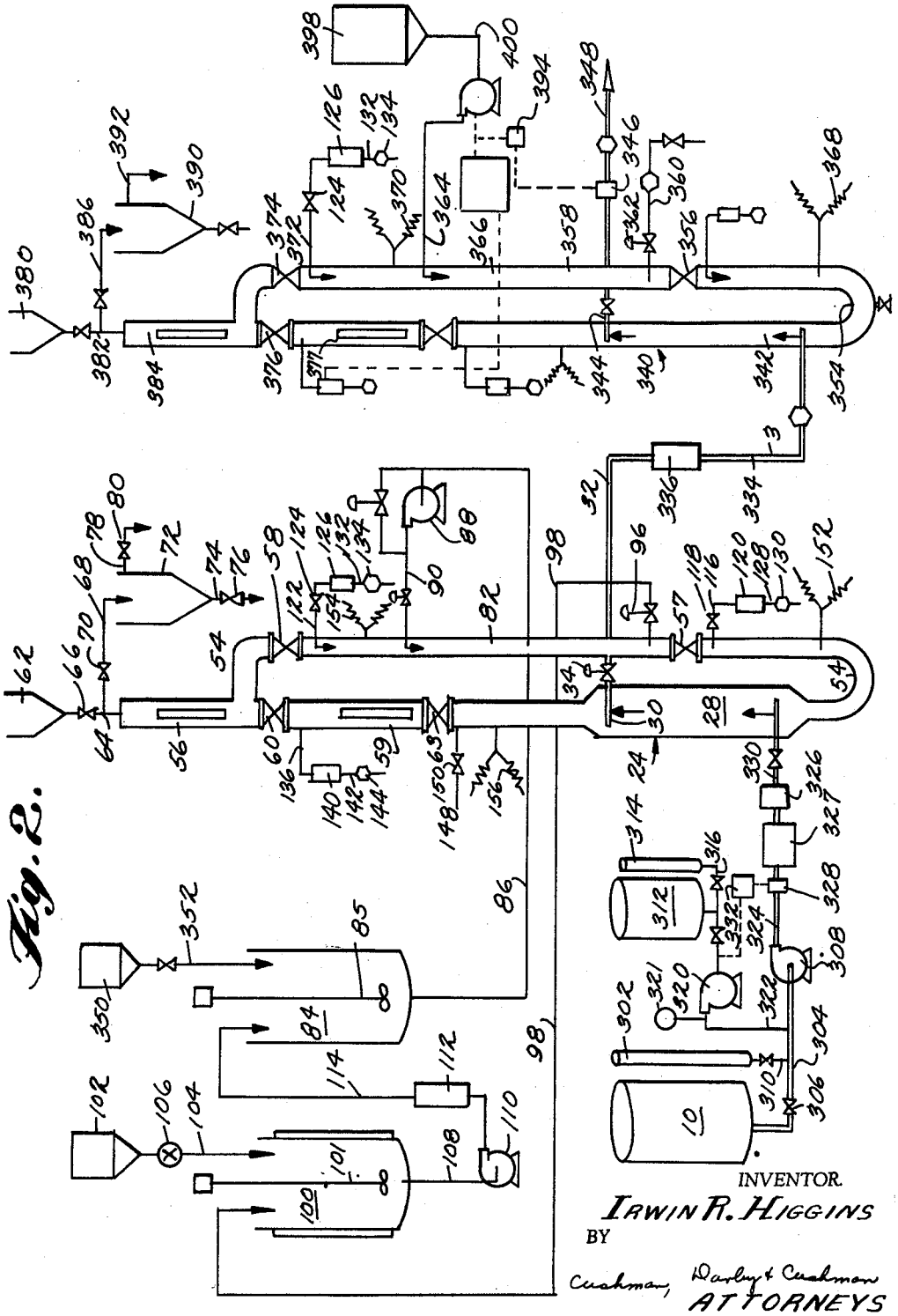


Fig. 2.

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RADIOACTIVE DECONTAMINATION OF MILK

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Fig. 3.

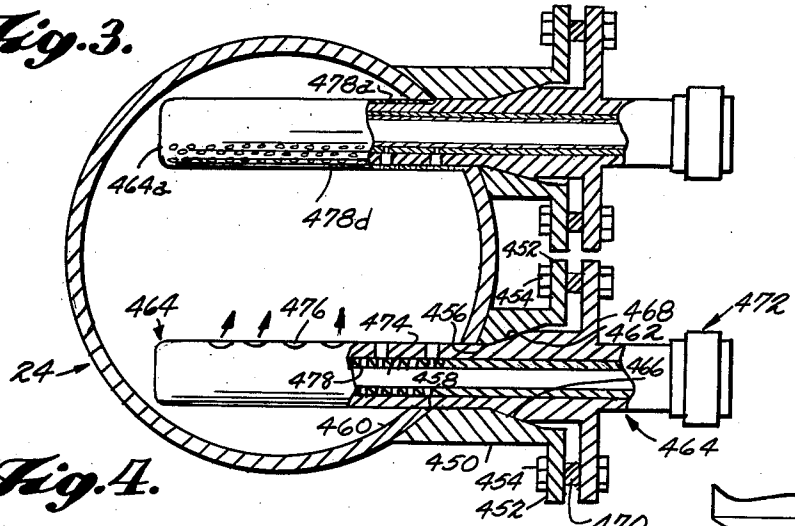
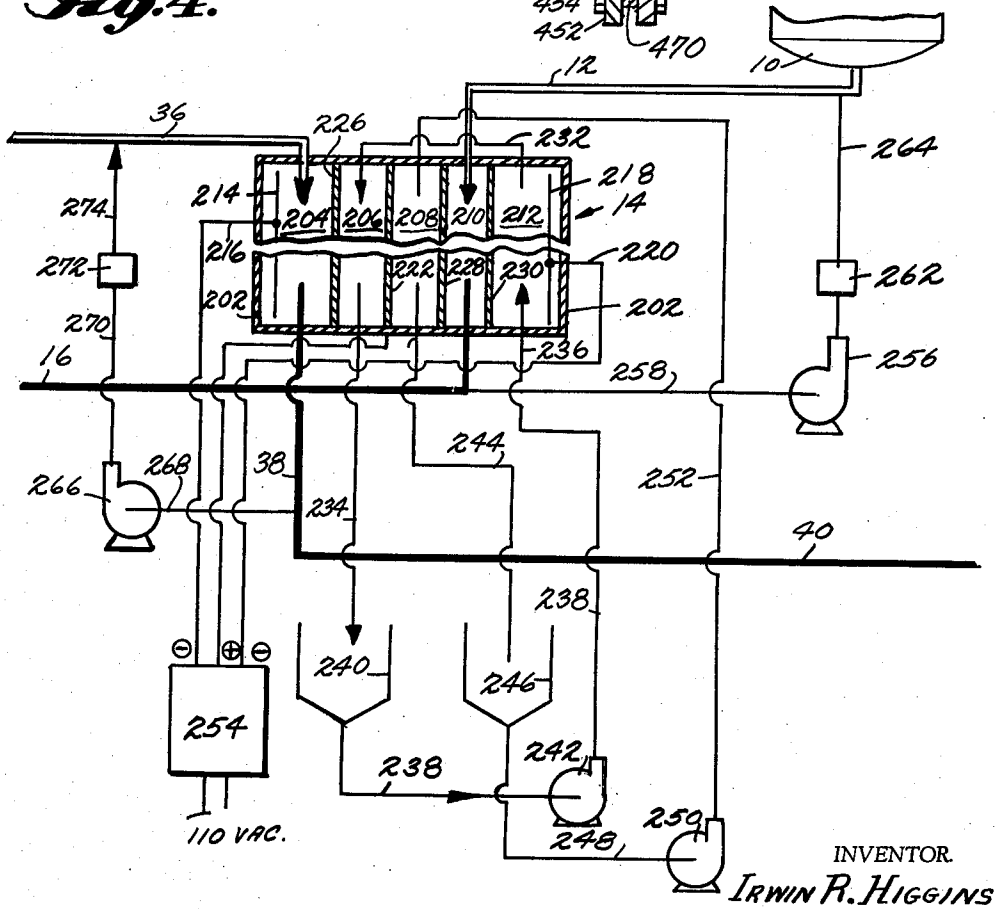


Fig. 4.



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RADIOACTIVE DECONTAMINATION OF MILK

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Fig. 5.

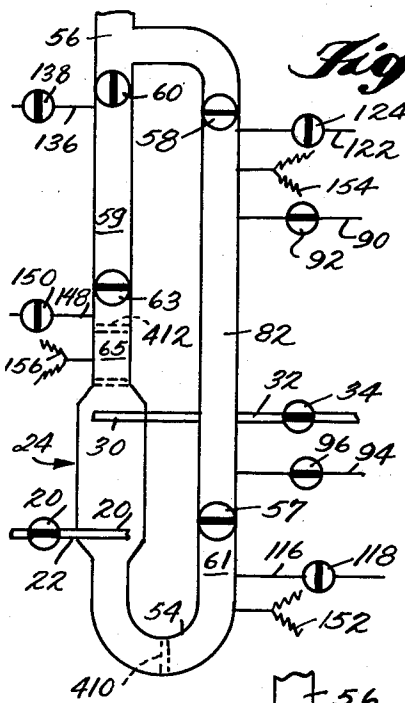


Fig. 6.

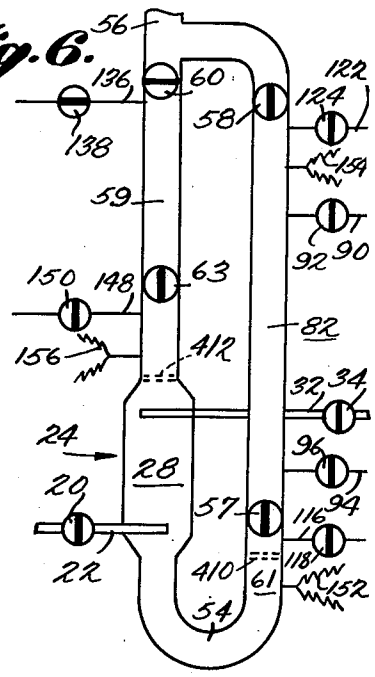


Fig. 7.

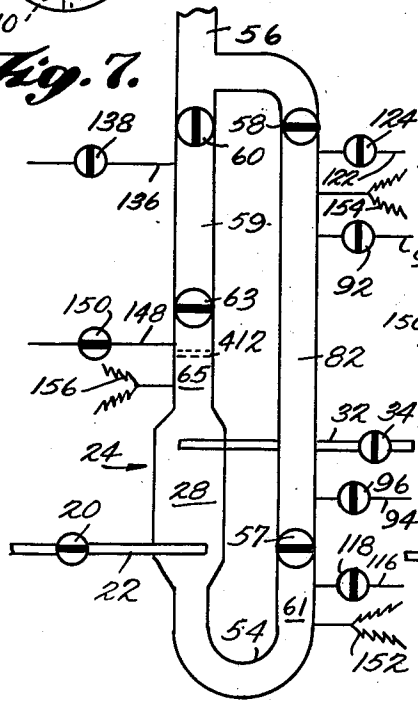
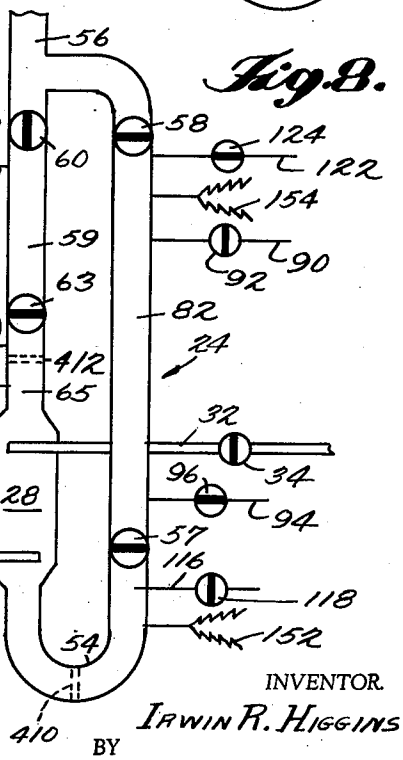


Fig. 8.



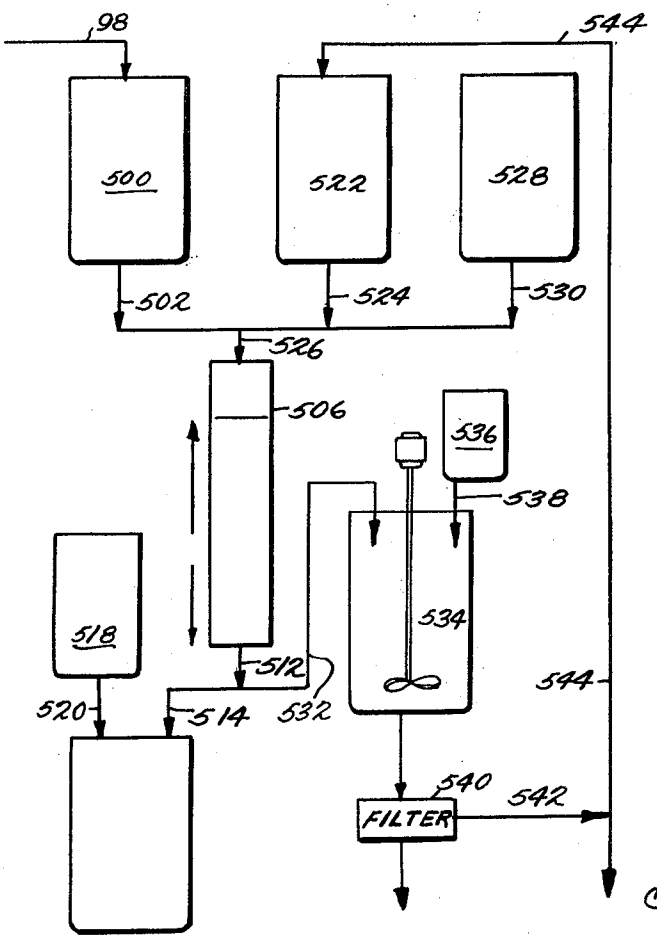
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RADIOACTIVE DECONTAMINATION OF MILK

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Fig. 9.



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United States Patent Office 3,194,663 Patented July 13, 1965

3,194,663 RADIOACTIVE DECONTAMINATION OF MILK

Irwin R. Higgins, Oak Ridge, Tenn., assignor to Chemical Separations Corporation, Oak Ridge, Tenn., a corporation of Tennessee

Filed Apr. 1, 1963, Ser. No. 269,585
10 Claims. (Cl. 99—60)

This invention relates to processes and apparatus for the treatment of milk, and, more particularly, for the radioactive decontamination of milk.

BACKGROUND OF THE INVENTION

It is well known that atmospheric nuclear explosions have produced radioactive fallout which has led to radioactive contamination of soil and plants. At one time, it was thought that only about 20% of the radioactive contamination in plants came from the soil, some 80% resulting from direct deposition from the air. Recent studies suggest, however, that soil is the source of perhaps as much as 50% or more of the radioactive contaminants in plants. Thus, radioactive accumulations in the soil will mean higher and higher radioactive levels in plants. The long half-life of some of the radioisotopes, especially strontium–90, indicates very slow radioactive decomposition and decay of the soil contamination. Even with no further atmospheric nuclear explosions, existing atmospheric radioactive fallout will continue for some time, and so long as radioactive fallout continues, soil contamination will increase and it is clear that radioactive contamination of soil, and thus of plants, will be a continuing unavoidable condition for an unknown future time.

Substantially all of the food ingested by man is derived from plant life or from animals which feed on plants. There is, then, a direct relationship between levels of radioactive fallout and food contamination in general. Contrary to common belief, there is no "threshold" or minimum level of fallout below which there are no harmful radioactive effects to man. Even small doses of radiation must statistically cause a certain incidence of disease, or physiological breakdown or harmful mutations. Moreover, the genetic effects of fallout on future generations are not precisely known. It has been reported, however, that even low levels have serious effects, and studies have even demonstrated the destruction of life at its inception in the mammalian fetus through complexing of strontium–90 isotopes in spermatozoa and leading to radiation decay of the chromosomes' structure. If strontium–90 contaminated food is consumed by mammals, this radioactive isotope also tends to be taken up by the bone marrow in the normal metabolic processes, and it remains there. The radiation activity in the bone marrow can especially cause anemia and severe illness, aside from the general damage induced by exposing the body to radioactivity.

It has been recognized that one of the likeliest sources for stronium–90 intake by humans is through milk. This is largely the result of the natural processes whereby cows form milk—strontium–90 in the soil being taken up in the plants of the pasture, then eaten by the cow, and thence forming a natural constituent of milk.

Some studies indicate that between 65% and 85% of the strontium–90 found in human bones is due to milk consumption. Other cationic radionuclides occasionally found in milk include barium–140 and cesium–137. The only anionic type of radionuclide observed in measurable amount is iodine–131. In cow's milk, 90 to 100% of the iodine–131 is in inorganic form as the iodide ion and the remainder is bound with the proteins. While iodine–131 has a comparatively short halflife of about eight days, its selective accumulation in the thyroid gland produces an unusual biological risk. This is especially true with the smaller glands of children.

A really useful process for removing radioactive materials from milk requires not only effective removal of the radionuclides but also that the milk be substantially unaltered in its make-up. A technique is required which is itself non-toxic, sanitary, and economically feasible. Chemical alteration is preferably held to at most a minimum, because chemical additions and/or removals add expense and tend to upset the rather delicate balance of milk constituents and produce taste changes. Without satisfactory taste in the decontaminated milk, the product will have little acceptance by the consumer regardless of other benefits (except, of course, in emergency situations of extraordinarily high radioactive levels).

The problem is to take out the undesired species without upsetting the normal balance of milk components. The normal cations in milk are potassium, sodium, calcium, magnesium, and smaller quantities of iron. The normal anions in milk are citrate, sulfate, phosphate, and chloride. These are the important constituents as far as ion exchange is concerned but milk also contains, of course, protein, casein, sugar, and fats, and these must be left substantially unaffected.

It has already been proposed to decontaminate milk by using an ion exchange technique to remove selectively strontium–90 as described in U.S. Patent 3,020,161. That process added an edible organic acid (citric acid or lactic acid) to lower the milk pH from about 6.6–6.8 to a level of about 5.2 to 5.4, and then passed the milk through a fixed bed ion exchange resin, selectively removing strontium cations from the milk. Thereafter, the pH was returned to the normal level. This process only partly solved the milk decontamination problem. Foreign components were still introduced into the milk and consequently the composition of the treated milk was altered in ways other than through the single removal of strontium–90. This process is also prohibitively slow and requires large amounts of ion exchange resin. Fixed bed ion exchangers involve, of course, batch operations and are not continuous. To adapt fixed bed ion exchange operations to a dairy system, multiple tank systems are required complicating the equipment and its operation with increased capital and operating costs (e.g. regenerate salt costs are higher than with the more efficient continuous countercurrent system).

OBJECTS OF THIS INVENTION

As its principal object, this invention provides a process which overcomes the disadvantages of the prior art, and which makes routine decontamination of radioactive milk realistically attractive for the first time.

Specifically, this invention provides for a novel and improved process and apparatus for the rapid and economical removal of the radioactive strontium–90 and iodine–131 isotopes from milk, with at most minimal alteration of the decontaminated processed milk.

More particularly, it is an object of this invention to provide a system for the removal of strontium–90 and iodine–131 from milk in which moving bed ion exchange columns are employed for the sequential removal of first the strontium–90 and secondly the iodine–131 contaminants, with continuous regeneration of the ion exchange resin employed in the columns, as needed. This apparatus also includes means preventing undesired contamination of the milk under process, and the system includes means for adjusting the pH of the raw milk to afford optimum removal of the radioisotopes, and for restriction of the pH after decontamination to the normal level.

It is, therefore, also an object of this invention to provide a milk decontamination system with pH adjustment means including an electrolytic cell having ion exchange resin membranes therein and adapted for automatic control and pH adjustment of the milk before and after decontamination. As still a further object, this invention also provides a pH adjustment technique in which a strong mineral acid is employed to decrease the pH of the raw milk, and a moving bed is employed to restore the normal milk pH.

The automatic controls and operation of the system of this invention, and other objects thereof, will now be more fully set forth in the following description.

DESCRIPTION OF THE DRAWINGS

In the drawings, FIGURE 1 represents, schematically, a milk decontamination system using an electrolytic pH adjustment technique and a moving bed ion exchange resin column loop according to one embodiment system of this invention.

FIGURE 2 illustrates, schematically, another embodiment system of this invention for the decontamination of radioactive milk in which two moving bed ion exchange resin column loops are employed and pH adjustment is through the use of a strong mineral acid.

FIGURE 3 is an illustration, partly in section, of the apparatus for introduction and distribution of milk into the moving bed ion exchange resin columns, and which may be employed in connection with any of the embodiment systems of this invention.

FIGURE 4 illustrates, schematically, and in greater detail, the electrolytic cell pH adjustment system which may be used according to the invention and as is illustrated in connection with the system shown in FIGURE 1.

FIGURES 5, 6, 7, and 8 schematically illustrate a portion of the ion exchange system provided by this invention during various stages of the operation.

FIGURE 9 illustrates schematically a regenerating solution recovery system also provided by this invention.

GENERAL DESCRIPTION OF THE INVENTION

According to the present invention, contaminated raw milk to be purified is first adjusted to the desired pH level of between 5 and 6, preferably between 5.2 and 5.4, either by addition of hydrochloric acid or by an electrolytic cell.

About half of the strontium–90 in milk is normally tied up with the proteins so that it is unavailable for ion exchange, when the milk is at its normal pH of 6.6 to 6.8. If the milk is acidified slightly, down to pH 5.2 to 5.4, this bound strontium is released and becomes available for ion exchange. Then about 95–96% of the strontium may be removed. The pH of 5.2 is, however, still not acid enough to precipitate the casein as normally happens when milk sours and curdles because of lactobacillus growth. Hydrochloric acid is used in this process for reasons which will be described later.

The acidified milk is then passed through an intermittently moving bed of a strong acid sulfonated polystyrene cation exchange resin in a continuous ion exchange column loop system equipped for decontamination, washing, and regenerating stages. Successive portions of resin are maintained in contact with successive portions of milk flowing therethrough for a period of time only sufficient to remove the strontium–90 and other cationic radionuclides therefrom. Fortunately, strontium–90 has a high selectivity factor of about 50 in the presence of interfering cations in milk (potassium, sodium, calcium, and magnesium). In the regeneration section of this apparatus, successive portions of the resin, previously used to decontaminate the milk, are regenerated and washed free from the radioactive cations with a controlled composition salt solution, and prepared for further decontamination uses. In order to prevent imbalance of the normal salts, the cation exchange resin is converted to a form whereby these cations are in the same ratio as they exist in milk. Strontium–90 is removed from the cation exchange resin with a stronger mixture of chloride salts of potassium, sodium, calcium, and magnesium. A composition is chosen which leaves the proper balance of these cations on the resin. The waste salt solution containing the strontium–90, barium, and cesium may then be disposed of.

In the system of this invention, means are provided to maintain the milk in the exchange column free from mixing or adulteration with the washing and/or regenerating solutions while maintaining an at most only very small loss of milk volume.

Subsequent to the cation exchange treatment, the milk is further processed to restore its original pH level and to remove radioactive iodine–131 content, using an anion exchange resin. Radioactive iodine is in a sense a less dangerous contaminant than strontium–90 because of its much shorter halflife; however, it can be present in significant and dangerous quantities and its removable is desirable in a scheme for the complete decontamination of milk. This step can be integrated, in the present invention with the pH readjustment step, so that both steps are achieved in one operation.

Fortunately, iodine has an extremely high affinity for the resin—much higher than the other anion components of milk. In order to prevent upsetting the anion composition, the anion exchange resin is preconditioned with a mixture of chloride, phosphate, and citrate that will leave these components on the resin in the same ratio as they occur in milk. It was found that, when citric acid was added to the milk, the anion exchange resin selectively removed chloride, probably because hydrochloric acid is a stronger acid; therefore, hydrochloric acid is used for acidification and hydrochloric acid is removed by the anion exchange resin. The anion exchange resin is partially converted to the hydroxide form with dilute sodium hydroxide and removes the most weakly absorbed anion, the chloride. By a stoichiometric counterflow of hydroxide form anion exchange resin and acidified milk, the free acid is all removed and the pH of 6.6 to 6.8 is restored.

At the same time, the trace of iodine–131 is strongly attached to the resin and it is not removed by the sodium hydroxide regeneration solution. The iodine–131 affinity for the resin is sufficiently high that its removal is not necessary since iodine–131 has an eight-day halflife. The maximum build-up of iodine on the resin, therefore, occurs in eight days. About 90% of iodine in milk occurs as iodide. The remaining 10% is tied up with the proteins that is not available for ion exchange. Therefore, about a 90% extraction is a maximum that can be expected. It has been found important to keep the iodine in the form of iodide. Iodide ion is very easily oxidized to elemental iodine by aeration or by chlorine water which may be used in equipment cleaning. Elemental iodine seems to have an affinity for some component of the milk, probably the fats and proteins. Iodine may be kept in the form of iodide by using a reducing agent for cleaning, such as SO_2, or by adding small amount of sodium sulfite in the sodium hydroxide regeneration stream.

It can be seen that the present invention provides a system comprised of several components adapted for and used in interdependent combination to achieve the overall objective. The description of several embodiments of this system now follows.

DETAILED DESCRIPTION OF FIGURE 1

In the drawings, FIGURE 1 illustrates a system for the decontamination of radioactive milk as provided by the present invention. A milk feed and supply tank 10 is provided of sufficient capacity to receive and have mixed therein a quantity of milk of perhaps 100,000 pounds per six-hour period, as provided at the dairy. Means, not shown, are provided for mixing of the milk in the tank, and for maintaining the tank at a temperature of about

38° F. The mixing is important in order that the natural variations in the milk composition and acidity from various cows, is minimized during the decontaminating processing thereof. This is an assist to the efficiency of the overall process, as will be mentioned hereinafter. It is important to maintain the milk at a temperature of about 38° F., as is well known, to inhibit bacterial activity and prevent spoilage, while not overcooling the milk.

The milk from holding tank 10 is delivered through line 12 to an electrolytic pH adjustment cell generally designated as 14, and leaves the cell after its pH is adjusted to a more acidic level via pipe 16, under the action of positive displacement, stainless steel, sanitary milk pump 18. It is then delivered through valve 20 via pipe 22 into the continuous ion exchange column generally designated 24.

The milk enters ion exchange column 24 through distributing means 26 (one embodiment of which is more clearly illustrated in FIGURE 3, see accompanying discussion). Distributing means 26 is located at the lower end of the decontaminating section 28 of the column 24. Through the continuing action of pump 18, the milk delivered from distributor 26 into section 28 passes upward through the cation exchange resin which completely fills section 28 and then passes out of this section through collecting means 30 and pipe 32, provided with valve 34.

As shown in FIGURE 1, the milk then passes through pipe 36 again into the pH-adjusting electrolysis cell 14 and exits therefrom through pipe 38. The milk in pipe 38 has been restored to the original pH which it had in holding tank 10. The milk then passes through pipe 40, valve 42, and pipe 44 into the fixed bed anion exchange column 46.

In column 46, radioactive iodine–131 is removed from the milk by the anion exchange resin, and the milk is then delivered via pipe 48 and valve 50 into decontaminated milk storage tank 52.

Referring now more particularly to the continuous anion exchange column 24, and its construction, it will be seen that this column comprises a "loop" adapted for the intermittent circulation of anion exchange resin from and to the decontaminating section 28. This column is constructed in accordance with the principles disclosed and claimed in U.S. Patent 2,815,332, issued December 3, 1957, to the present inventor.

The continuous ion exchange column 24 shown in FIGURE 1 includes the decontamination section 28 which is arranged to permit downward flow of the resin from decontaminating section 28, and the resin regeneration section 82 arranged for upward flow of the resin. Resin circulating conduit 54 extends downwards from section 28 and then loops upwards and extends vertically alongside and to a level above the decontaminating section 28. It is also provided with resin valves 57 and 58, which control the flow of the resin in this portion of the loop of the column 24. Conduit 54 then opens into the upper resin reservoir 56 at orifice 58. Conduit 56 is also provided with two resin valves 60 and 62, which also serve to control the flow of the resin.

As shown, conduit 56 extends above communicating orifice 58 and is provided at its uppermost end with a resin reservoir tank 62, adapted to deliver additional ion exchange resin to the column 24 via conduit 64 controlled by valve 66. Pipe 68, controlled by valve 70, is arranged in communication with pipe 64 and is provided to permit overflow of waste wash water and resin fines into disposal tank 72, which has drain pipe 74 controlled by valve 76 and overflow lines 78 controlled by valve 80.

The section of the loop of column 24 located between resin valves 57 and 58 in conduit 54 is the resin regeneration section 82, and this section is provided to regenerate successive portions of resin which had previously been in milk decontaminating section 28, so that the resin may be again used, on recycling, for decontamination of further portions of the milk.

Regeneration of the resin is carried out with a specially-prepared make-up salt, as already mentioned, formed of calcium chloride, magnesium chloride sodium chloride, and potassium chloride such that after regeneration these cations will be on the resin in the same ratios that such cations naturally occur in milk. The following Table I illustrates typical relative proportions of these cations in milk, and the appropriate proportions of which would be used in the regenerating salt solution. The different ratios or proportions in the regenerating salt solution reflect differences in affinity of the cations for the resin.

Table I

Cation	Meq./l. Milk	Eq./l. Regenerating Salt Solution
Mg	8.5	.083
K	37.2	.385
Na	22.4	.217
Ca	50.0	.625

This regenerating salt solution is held in tank 84 equipped with mixing means, not shown, until required for resin regeneration. During the regeneration stage, the salt solution is delivered through pipe 86 and via pipe 88 through pipe 90 controlled by valve 92 into a regeneration section 82 of resin circulating conduit 54, at a point somewhat removed from and below resin valve 58. The salt solution flows downwardly through regeneration section 82 of conduit 54. The regenerating salt solution then leaves conduit 54 through pipe 94 controlled by valve 96 and passes via pipe 98 into treating tank 100. Tank 100 is provided with means to receive a co-precipitating solution stored in tank 102 and delivered through line 104 controlled by valve 106. In an operation described hereinafter, the radioactive strontium–90, and other reactive salts, removed from the milk in decontaminating section 28, and then stripped from the resin in regenerating section 82, are precipitated from the salt solution in tank 100. The solution from tank 100 then passes via line 108 and filter pump 110 through filter 112, which collects the radioactive strontium–90 precipitate. The filter element in filter 112 may then be removed from time to time as needed and suitably disposed of as radioactive waste, for instance by burial.

From filter 112, the now-decontaminated salt solution is delivered through line 114 into tank 84 where it is again available for use in regenerating the ion exchange resin. Resin circulating conduit 54 is also provided with water line 116 controlled by valve 118 and adapted to deliver water through water rotometer 120 into conduit 54. As shown, water pipe 116 enters into resin conduit 54 at a point below resin valve 57. A second water pipe 112, with rotometer 126 and controlled by valve 124, is arranged to enter section 82 just below resin valve 58 into rotometer 126. Line 128, controlled by valve 130, and line 132, controlled by valve 134, lead to water supply.

Resin return conduit 56 is also provided with water lines for delivery and removal of wash water. Pipe 136 controlled by valve 138 is provided for delivery of water through rotometer 140, with line 142 controlled by valve 144 connected to the water supply. Pipe 136, as shown, opens into conduit 56 at a point below resin valve 60. Conduit 56 is also provided with water outlet line 148 controlled by valve 150, for removal of waste wash water at a point between resin valve 62 and decontaminating section 28.

As a further and important feature of this invention, means are provided for the substantially automatic control of the operation of these various valves in the wash water and salt regeneration solution lines, in such a manner as to insure that the milk is not contaminated or

adulterated with either the wash water or the salt solution.

As an embodiment of these control means, there is shown in FIGURE 1 a conductivity probe 152 in resin circulating pipe 54 and arranged at a point below water pipe 116. A secondary conductivity probe 154 may be arranged in pipe 54 between salt solution pipe 90 and wash water pipe 122. A third conductivity probe 156 may be arranged in resin pipe 56 between water outlet pipe 148 and regenerating section 28 of the resin exchange column 24. Probes 154 and 156 can be eliminated and dilution of the regenerating salt solution compensated for by addition of dry salt mixture thereto (see infra).

These conductivity probes are responsive to changes in the conductivity of the solution in the ion exchange resin column 24 at their respective locations, and through an appropriate servo-mechanism actuate the respective line valves in response to such changes in conductivity measurements, as will be described more fully hereinafter.

The ion exchange resin column 24 is, finally, also provided with drain pipe 158 controlled by valve 160, in the event draining and removal of the entire column is desired for cleaning or other purposes.

DESCRIPTION OF FIGURE 4

FIGURE 4 illustrates, schematically, but in greater detail, the electrolytic pH adjustment cell 14 generally shown in FIGURE 1. As seen in FIGURE 4, raw milk from hold tank 10 is delivered through line 12 to the interior of electrolytic cell 14. This cell has a casing 202 which is divided into a series of compartments 204, 206, 208, 210, and 212. Arranged in each of compartments 204 and 212 is a cathode 214 and 218, respectively, connected to a suitable negative D.C. electrical source. An anode 222 separates compartments 206 and 208, and is suitably a Tirreloy anode connected by lead 224 to a suitable positive D.C. electrical source. A D.C. potential is maintained between the anode 224 and the cathodes 214 and 218 during operation of this cell.

Compartments 204 and 206 are separated from each other by an ion exchange resin membrane 226. Similarly, ion exchange membranes 228 and 230 respectively separate compartment 208 from compartment 210 and compartment 210 from compartment 212.

It is thus seen that this electrolytic cell 14 is generally divided into two cathode-anode cells, the lefthand side being composed of compartments 204 and 206, and the righthand side composed of compartments 208, 210, and 212. A current is imposed across each of these cells. Each of the five compartments 204–212 is filled with an electrolyte, as described more fully hereinafter, and there is, consequently, existing in the electrolytic cell 14 a current passing between the anode and each of the cathodes. As is well known, in electrolytic solutions, the cations tend to migrate to the cathode and the anions tend to migrate to the anode.

As shown in FIGURE 4, the raw milk for processing passes through only compartment 210 of electrolytic cell 14, being delivered through pipe 12 and withdrawn through pipe 16 for delivery to the ion exchange column 24 as shown in FIGURE 1. The decontaminated processed milk returning from the ion exchange column 24 via pipe 36 passes only through compartment 204 of cell 14 and is then withdrawn via pipes 38 and 40 for further processing in accordance with the system fully illustrated in FIGURE 1.

In the cell, compartment 212 contains an aqueous electrolytic solution preferably having a metal cation ration and concentration the same as milk, which cations (calcium, magnesium, sodium, and potassium) are conveniently introduced as chloride salts. (The salt balance, however, does not need to be precisely the same as in the milk since the process is reversible.) Ion exchange membrane 230 is a cation exchange membrane, and thus prevents passage of anions from compartment 212 into compartment 210; however, cations may pass from compartment 210 through the membrane 230 into compartment 212 and into contact with cathode 220.

Compartment 208, between anode 224 and membrane 228 contains a suitable acid solution serving as a source of hydrogen ions, and is preferably a citric acid solution (since citric acid solution is a convenient current-carrying solution and acceptable on edible grounds). Membrane 228 is also a cation exchange resin membrane serving to prevent passage of anions from the milk in compartment 210 into compartment 208 and anode 224, while permitting passage of cations.

It will thus be seen that cation exchange membrane 228 and the citric acid solution in compartment 208 serve to shield the milk in compartment 210 from the anode 224. This is important for otherwise the milk would be in contact with the acid-generating anode (tending to produce hydrogen ions) and would lead to local high acid concentrations with the possibility of curdling of the milk, unless special means were taken to define an appropriate anode which would not have such disadvantages.

Compartment 210 is, of course, filled with the raw milk delivered through pipe 12.

On imposing a D.C. current across anode 224 and cathode 220, cation migration will occur. This will involve passage of hydrogen ions from citric acid in compartment 208 through cation membrane 228 into the milk in compartment 210, in an amount equal to the removal of metallic cations (calcium, magnesium, sodium, and potassium) passing through cation exchange membrane 230 and into the anode-carrying compartment 212. The acidity (i.e., hydrogen ion concentration) of the milk in compartment 210 is thus increased and the catholyte solution in compartment 212 would gradually tend to become more alkaline.

Referring now to the lefthand side of electrolytic cell 14 and compartments 204 and 206, in this instance, the decontaminated milk passing into the cell through line 36, and coming from ion exchange column 24, travels through compartment 204 in contact with cathode 214, but shielded from anode 222 by ion exchange membrane 226 and compartment 206. There is no need to shield the milk from cathode 214.

The D.C. current imposed across anode 222 and cathode 214 again causes flow of cations from the anolyte solution in compartment 206 through the cation exchange memberane 226 towards the cathode 214, i.e. into the catholyte solution in compartment 204 which is simply the decontaminated milk. Thus, the metal cations removed from the milk in compartment 210 are returned to the milk in compartment 204, while the hydrogen ions formed in the milk in compartment 210 to increase its acidity, are replaced with the incoming cations in compartment 204. The current between anode 224 and cathode 214 is balanced with that between anode 224 and cathode 218. This insures the equivalent ion transfers, and the pH of the milk leaving the electrolytic cell through pipe 38 is the same as the pH of the milk entering the electrolytic cell 14 through pipe 12.

This invention also provides refinements in the basic cell system of the electrolytic cell just described. For instance, as schematically shown, compartments 206 and 212 may be equipped with pipes 232, 234, 236, and 238 which are also provided with surge tank 240 and circulating pump 242. The catholyte solution in compartment 212 may thus be maintained identical in composition with the anolyte solution in compartment 206, and is, in fact, the same solution, by constant circulation thereof.

This circulation is important in order to prevent the localized precipitation of magnesium hydroxide, and other hydroxides, which would otherwise tend to occur in compartment 212 as the catholyte solution therein became increasingly alkaline during the processing of the milk. Similarly, if not circulated, the anolyte solution in compartment 206 tends to become acid during processing of

the milk, as its alkaline cations are removed through membrane 226 and delivered to the milk passing through compartment 204. By circulating the solutions in compartments 206 and 212, these changes in the solution are nullified and balanced out, and consequently the respective solutions in compartments 206 and 212 remain essentially the same.

This is, further, an important feature of the system for maintaining relatively constant current densities in both sides of electrolytic cell 14. This permits maintaining of the pH in the milk leaving the cell, through either line 16 or line 38, singly by control of the power input. It has also been observed that there is substantially no effect on the pH in the milk as it travels through the ion exchange column 24, and this also permits the above-described operation of electrolytic cell 14.

Furthermore, the cation exchange membranes 226 and 230 are substantially identical membranes, and consequently it is unnecessary, in the practice of the system provided by this invention, to particularly control the nature of the cation which is removed from the milk in compartment 210 (and replaced by a hydrogen ion as the milk is acidified); nor is it important or necessary to be concerned with the particular cation which is returned to the milk in compartment 204 as its pH is again raised to a normal level. This is so because the electrolyte solution in compartments 206 and 212 is the same and the ion exchange membranes 226, 230 are the same and the current densities are balanced, and, consequently, whatever metallic cations were removed from the milk in compartment 210 can be expected to be replaced in the same quantity and ratio in the milk in compartment 204. That is, any selective migration tendency of the cations (magnesium, calcium, sodium, and potassium) through the membranes 226 and 230 balances out.

It will be appreciated also that the ion exchange resin membranes 226, 228, and 230 are not employed as ion exchangers in this cell system, but as ion migration barriers instead. They are used for conductivity and to prevent the migration of anions from one compartment of the cell 14 to another.

It has also been found further advantageous to recirculate the citric acid anolyte solution in compartment 208 to minimize polarization for the same reason the other electrolytes were circulated and to remove decomposition gases. As shown, it may be withdrawn through line 244 into surge tank 246 and then delivered via line 248, pump 250, and line 252 again to compartment 208. This also minimizes any possible alterations in the citric acid anolyte solution during operation, and permits the cooling of the same, should any increase in temperatures as a result of reaction heating occur.

It will also be appreciated that circulating pumps 242 and 250 are employed at least in part as agitators to constantly induce turbulence into the electrolyte solution to insure good conductivity, as well as insuring homogeneity and proper balancing of the solutions.

The D.C. power input to cell 14 is conveniently provided by a dual output rectifier schematically shown at 254. This rectifier is also advantageously arranged to be responsive to pH sensing units which constantly sense the pH of milk sampled from pipes 16 and 38. For instance, in FIGURE 4, pump 256 is arranged to withdraw, continuously or intermittently, samples of milk from pipe 16 through line 258 and to deliver the same through line 260 into the pH sensing device 262 (which may be any well known pH measuring electrode system). If the pH of the sample falls above or below the desired level, a signal is then transmitted to the dual output rectifier 254 to decrease or increase the current in the right side of the electrolytic cell 14. Milk passing through the pH sensing device 262 is returned via line 264 to supply pipe 12, so that no milk losses occur in this operation.

Similarly, pump 266 withdraws milk samples via line 268 from pipe 38, and delivers the same through line 270 to pH sensing unit 272. Again, this pH sensing unit will signal the rectifier 254 if the pH of the milk sampled at line 238 is too high or too low to cause an increase or decrease, as required, in the current density in the lefthand side of the cell 14. The milk sample is returned through line 274 to delivery pipe 36, again with no losses in the sampling process.

Providing such means as have been just described for independent control of the current density in the two sides of cell 14 is of value particularly in those cases that the raw milk delivered to the unit varies significantly in pH over a day's milking operation. It is well known that cow's milk, even from cows of the same breed and grazing on the same pasture, can vary by several tenths of a pH, and from cow to cow. Particularly in installations where hold tank 10 may be of relatively small capacity, sufficiently large variations in raw milk pH can occur such that adjustment of the current density in cell 14 is required as a practical matter to insure that the optimum pH for radioactive cation decontamination in ion exchange column 24 is achieved.

It is also possible, of course, to employ two separate cells, one corresponding to the right half of cell 14, and one corresponding to the left half of cell 14, but not sharing a common anode. An inverse arrangement with a common cathode can also be used. All other operations and features remain the same.

It can thus be seen from the above discussion of electrolytic cell 14, that the raw milk to be processed may have its acidity adjusted to a lower pH preliminary to the decontaminating ion exchange treatment, and thereafter the acidity can be restored to its normal higher pH level without the introduction of any foreign chemicals or materials into the milk. Except for the removal of the radioactive cationic material, and the replacement of those cations by other metallic cations taken up from the resin by the milk during its passage through decontaminating section 28 of column 24, the milk delivered from electrolytic cell 14 through lines 38 and 40 is the same in its chemical composition and make-up as the milk originally delivered to the electrolytic cell 14 through line 12.

DETAILED DESCRIPTION OF FIGURE 2

FIGURE 2 of the drawings illustrates another embodiment of this invention, and presents features which are not shown in the system illustrated in FIGURE 1. It will be appreciated, however, that various components of the system in FIGURE 2 may be used with the system in FIGURE 1, and vice versa, as will be brought out hereinafter. Insofar as seems practicable, the same element numbers employed in FIGURE 1 will be employed for like elements in FIGURE 2 in the following discussion thereof.

In FIGURE 2, milk from storage tank 10, equipped with sight glass 302 communicating through valved line 310, is drawn through pipe 304, controlled by valve 306, by pump 308. Reservoir tank 312, equipped with sight glass 314 communicating therewith via valved line 316, is arranged to deliver an approximately one molar hydrochloric acid solution through valved line 318, under the action of pump 320 and through line 322 into pipe 304. The hydrochloric acid solution in tank 312 may be more concentrated and means 321 provided for admixing water therewith at pump 320 to the correct dilution at agitator pump 308. The acidified milk then passes via pipe 324 to a pH sensing cell 328, thence to a hold tank 327, and finally through a filter clarifier 326 and by valved pipe 330 into the cation exchange resin column 24 at the bottom of the decontaminating section 28 thereof.

Hold tank 327 is of adequate capacity to provide a 15 to 30 minute delay for the acidified milk prior to ion exchange. This delay has been found to be important in order to permit the strontium–90 to be completely re-

leased from complexes with the protein content of the milk. Clarifier 326 removes any small amount of curd formed by localized precipitation during the acid addition.

The pH sensing flow cell 328 constantly measures the pH of the milk flowing through pipe 324, and its signal is delivered to the pH control servo-system, schematically shown as 332, which in turn controls the speed of pump 320. By this arrangement, the quantity of hydrochloric acid delivered to the milk in pipe 304 from reservoir tank 312 is constantly and automatically controlled to maintain the desired pH level of about 5.2 to 5.4 for optimum radioactive cation removal in decontaminating section 28.

As in column 14 in FIGURE 1, the milk passes upwardly through the decontaminating section 28, in FIGURE 2, and then is conducted out of column 24 via pipe 32. In this system of FIGURE 2, however, the milk in pipe 32 is not deacidified as in FIGURE 1. Instead, the milk is delivered through valved pipe 334, and optionally through a cooling heat exchanger 336, into a second ion exchange column 340, containing an anion exchange resin.

As shown in FIGURE 2, the acidified but radioactive cation-decontaminated milk passes upwards through a combined deacidification and radioactive anion decontaminating section 342 of column 340 and is then collected and removed through valved pipe 344, again passing through a pH measuring flow cell 346, and is then delivered from pipe 348 to a receiving tank, not shown.

The milk delivered from pipe 348 is decontaminated and deacidified milk with its iodine–131 content also removed, as will be explained more fully hereinafter.

Referring again to the apparatus and system associated with column 24, in FIGURE 2, a regenerating salt stripping solution is again provided with cooling-jacketed precipitating tank 100 and agitating-make-up delivery tank 84. Each of these tanks is fitted with a suitable mixing means schematically shown as 101 and 85, respectively. Tank 100 is also equipped with a reservoir 102 adapted to deliver a suitable strontium–90 precipitating solution to the contaminated recycled regenerating salt in tank 100, through line 104 controlled by valve 106.

As shown in FIGURE 2, and as arranged in FIGURE 1, the regenerating salt solution is withdrawn from the regenerating section 82 of column 24 through line 98 controlled by valve 96. This solution, which contains the radioactive strontium–90 stripped from the cation exchange resin in column 24 (which strontium–90 had, in turn, been removed from milk in decontaminating section 28) is then agitated in tank 100 and the strontium cations are precipitated, as in the system of FIGURE 1, and as will be more fully related hereinafter. The solution from tank 100 is withdrawn through line 108 via pump 110 and delivered to filter 112 wherein 90% of radioactive strontium–90 is removed.

The now-decontaminated regenerated salt solution is passed through line 114 into tank 84. This tank is provided with a second reservoir vessel 350 which is arranged to deliver through valve line 352 whatever regenerating dry salt mixture or concentrated salt solution is required to make up dilution occurring during operation of the overall scheme. The regenerating salt solution is then delivered through line 86 by means of pump 88 through line 90, and into column 24 at the top of regenerating section 82.

As will be seen, and as already related in connection with the description of column 24 in FIGURE 1, the regenerating salt solution passes downwardly through regenerating section 82 of column 24 to a point where it is withdrawn through line 98 and recycled as just described.

The anion exchange column 340 is constructed similarly to cation exchange column 24, although as shown, and for reasons which will become clear, its combined anion-decontaminating and deacidifying section 340 is of lesser volume than the cation-decontaminating section 28. Conduit 354 extends downwardly from decontaminating section 342 and then loops upwardly to resin valve 356. The portion of conduit 358 between drain line 360, controlled by valve 362, and regenerating alkali solution supply line 364 is the anion exchange resin regenerating section 366. Conductivity probes 368 and 370 are arranged similarly to conductivity probes 152 and 154 (in column 24) as is valved wash water supply line 372 which enters column 340 at a point below resin valve 374.

In the other portion of the loop of column 340, above decontaminating section 342, resin valves 376 and 378 are arranged similarly to resin valves 60 and 63 in column 24. Again, also, a reservoir supply tank 380 is arranged for introduction of make-up resin through valve line 382 into the upper portion 384 of column 340; and line 386 is arranged to permit overflow of waste water, from which resin fines may be collected in settler tank 390, the waste water being removed through line 392.

As an important feature of the system, anion exchange resin column 340 may be provided with pH servo-control means 394 which are responsive to the pH sensed by flow cell 346, and, in turn, control the resin flow rate and the operation of pump 396. This pump is arranged to withdraw an alkali solution from reservoir tank 398 through line 400 and delivery to regenerating section 366 through line 364. The pH servo-control 394 linkage with pump 396 and the resin movement system is arranged so that the quantity of alkali delivered to the regenerating system is balanced to conform with the resin movement to maintain the pH of the decontaminated deacidified milk which is removed from decontaminating section 342 of column 340. An increase in resin movement will tend to increase the alkalinity of the milk.

THE DESCRIPTION OF THE OPERATION OF THE CONTINUOUS ION EXCHANGE COLUMNS

The various continuous ion exchange columns in the system of this invention are operated in essentially the same manner. While the following description will refer particularly to column 24, it will be understood that it is equally applicable to column 340. For simplicity, this description will be made in connection with FIGURES 5–8, which are adapted for schematic illustration of the positioning of the various valves involved in the operation, to facilitate a better understanding of the same.

Referring first to FIGURE 5, this illustrates the condition of ion exchange column 24 during the decontamination/regeneration cycle when milk is flowing upwardly through decontaminating section 28, and a separate portion of the ion exchange resin is being regenerated in regeneration section 82. As seen in FIGURE 5, during this cycle, resin valves 57, 58, and 63 are closed, and resin valve 50 is open. Valves 20 and 34 in pipes 22 and 32, respectively, are opened, permitting milk flow through decontaminating section 28. Valves 92 and 96 in regeneration salt lines 90, 94, respectively, are also opened, permitting downward flow of the regenerating salt stripping solution through section 82. Valves 118 (line 116), 124 (line 122), 138 (line 136), and 150 (line 148) are all closed.

As already mentioned, after a predetermined time of passage of milk through the decontaminating section 28, and in accordance with the principles described and claimed in U.S. Patent 2,858,222, the column 24 is operated so as to shift and replace the ion exchange resin bed contained therein by introducing a fresh portion of regenerated resin.

To effect this procedure, resin valve 60, milk pipe valves 20 and 34, and regenerated salt solution line valves 92, 96 are all closed. Resin valves 57, 58, and 63, and valve 138 in hydraulic water supply line 136 are all opened, introducing a hydraulic thrust therethrough line 136 at the top of lower resin reservoir 59. Valve 150 on line 148 remains closed to prevent any water outlet flow at

that point. The condition of the valves during this cycle is shown in FIGURE 6.

The hydraulic thrust is applied in section 11. The resin in the reservoir is pushed around the stainless steel loop, water and resin are pushed into water elimination section 64, milk and resin are pushed into feed rinse section 61, water is pushed into regenerating section 82, regenerated salt solution is pushed into regeneration rinse section 83 and water and resin are pushed into upper resin reservoir 56. As shown in FIGURE 6, the milk/water interfaces 410 and 412 have also been moved about the loop along with the resin.

In the next step, valve 138 in hydraulic water supply line 136 is closed, resin valves 57, 58, and 63 are closed and resin valve 60 is open. The resin that had been pushed into upper reservoir section 56 drops into lower reservoir section 59. Valve 20 in milk line 22 is now opened along with valve 150 in water line 148. As milk flows into decontaminating section 28, the milk/water interface travels upwards into water elimination section 65. Conductivity probe 156 in section 65 senses the lower conductivity of water and prevents milk from being transferred out of the column through line 32 by maintaining valve 34 closed (see FIG. 7). When milk hits the conductivity probe in section 65, this closes valve 150, stopping the outlet of water through line 148, and valve 134 is opened to allow the processed milk to leave the column through line 132.

Milk will also have surrounded conductivity probe 410 in said rinse section 61, which senses the increased conductivity and signals water to enter section 61 through line 16 by opening valve 118. Valve 118 is closed and the water flow ceases when the conductivity indicates that water is contacting the conductivity probe 152. In similar manner, the conducting regenerating salt solution in section 83 is rinsed out with water admitted through line 122 and conductivity probe 154 indicates when the water/regenerating solution interface has passed below it (see FIG. 8). This conductivity control of waterflow in the column loop prevents dilution or loss of milk not going through the ion exchange column loop and also prevents dilution of the regenerating salt solution.

In the next step valve 138 in hydraulic water supply line 136 is closed, resin valves 57, 58, and 63 are closed, resin valve 60 is opened, and the resin that had passed into section 56 drops into lower reservoir section 59. Valve 118 in water supply line 116 is opened, along with valve 150 in water outlet line 148. The conductivity probe 156 in section 65 senses the low conductivity of water and prevents milk from being transferred out of the column but allows it to be pushed counterclockwise and up through section 65 to displace water that came in with the resin, water being admitted through line 116 for this purpose (see FIG. 7).

Valve 124 is now closed and valve 92 opened for cycling of the regenerating salt solution through regenerating section 82, the same being introduced through line 90 and withdrawn through line 94. After expiration of the established decontamination period, the resin movement cycle is thereafter repeated through the steps just described in connection with FIGURES 5, 6, 7, 8, etc.

An important part of this system lies in the use of the conductivity probes 152, 154, and 156, to detect the position of the various interfaces between different liquids in the column, and prevent dilution or loss of milk, and also prevents dilution of the regenerating salt solution. While there is a certain disturbance of the ion exchange resin in the column during its intermittent movement from one place to another, it has been found that the milk/water interface forms a definite boundary between the two solutions. Because of this phenomenon, it has been possible to maintain safeguards to prevent adulteration of the milk by inadvertent admixture thereof with water or the regenerating salt solution.

It will also be understood that it is a preferable feature of this invention to arrange automatic valve cycling in response to the basic time schedule and the sensing response of the respective conductivity probes. Thus, conductivity probe 156 may be arranged with suitable solenoid valves 150 and 34 so that valve 34 will remain closed and valve 150 will remain open until the milk/water interface 412 is above probe 156, but should the interface fall below probe 156, valve 34 is automatically closed and valve 150 is automatically opened.

During the cycling operations of the resin, as just described, it will be understood that the introduction of the rinse and pulse water into the column is accommodated through the overflow means 68 (FIGURES 1 and 2) above delivery conduit 56. Some resin fines may be carried with this water overflow, and to permit recovery of the same, settling tank 72 is provided, so that waste water overflows through line 78 and recovered resin fines may be removed from time to time through line 74 by opening line 76.

Attrition of the resin during the operation is made up through supply of additional resin, as required, from reservoir 62, as already mentioned.

Another feature of this system is that the milk flow is introduced and maintained through the operation of only one pump (pump 18 in FIGURE 1, pump 308 in FIGURE 2); and the regenerating salt solution flow is also maintained through the operation of but a single pump (pump 88 in FIGURES 1 and 2 for column 24, pump 402 for column 340 in FIGURE 2).

DESCRIPTION OF THE CATION EXCHANGE RESIN REGENERATION CYCLE

In connection with column 24, as shown in FIGURES 1 and 2, and as already mentioned, the cation exchange resin in section 82 is regenerated by treatment with a cation salt solution delivered from tank 84 through line 86 by the use of pump 88. This is a balanced salt solution of calcium, magnesium, sodium, and potassium chlorides at a concentration of 1.11 to 1.51 normal, preferably about 1.31 normal, and displaces the strontium 90 content on the cation exchange resin (acquired in decontaminating section 28, from the milk). This regeneration stage requires about 3.5 to 4.5, usually about 4 volumes of salt solution per volume of resin.

While this salt solution is then disposed of by dumping to the drain, practical operation of the system of this invention would not be desirable absent suitable means for disposal of the strontium–90 content stripped from the resin. The mixed chloride salts are the most expensive reagents used in the whole operation, and it is also desirable to separate the strontium–90 from the solution for more compact disposal or for transfer to a burial ground rather than dumping back into the water stream.

One method provided by this invention is to add stable isotope of strontium chloride to the chloride salt solution in quantities of about 3 to 4 grams of strontium per liter in tank 100. Sulfate ion is added as calcium sulfate slurry in order to limit the amount that goes into solution. This calcium sulfate slurry is made at about 10 grams per liter and only about 3 grams per liter goes in solution. This slurry is stirred and heated to about 85–95 degrees C. and held for from about 1 to 2 hr., preferably about one hour. About 90% of the strontium–90 is thusly coprecipitated with the strontium and calcium sulfates. This slurry is then filtered through filter 112 to yield approximately 25 gallons of filter cake, per 1250 gallons salt solution, which is then ready for disposal. The treated salt solution has been slightly diluted and it is recommended that about 10–20% be discarded. A fresh mixture of dry salt is added in tank 84 to make up the required solution volume and concentration for the next regeneration. By adding dry salts, an evaporation step to maintain concentration may be avoided.

This recovered salt solution may contain about 0.6

gram per liter of strontium, as essentially non-radioactive strontium chloride. Most of this will stay in the salt solution, of course, but a small fraction may be picked up by the resin and the stable isotope of strontium in milk (Sr–88) may be increased slightly. The normal concentration of strontium in milk is about 1 mg. per liter. It is calculated that this precipitation method would at most contribute about 5 mg./liter to the milk.

DESCRIPTION OF FIGURE 9

Another method for removing strontium–90 from the regenerating salt solution is to run this solution through a fixed-bed cation exchange resin of a higher cross linkage than that used for the milk, which will have a higher affinity for strontium-90. Used salt is delivered through line **98** to tank **500**, and then passed down through lines **502**, **504**, and through a bed of resin, e.g. Dowex–50–W, X-12—50–100 mesh in perhaps a 24 cu. ft. bed. Eighty percent of the solution may be passed through lines **512**, **514** into tank **516**, with only about five percent breakthrough of the strontium–90. This salt is then ready for reuse with a twenty percent makeup of fresh or mixed salt from tank **518** through line **520**. This method has the advantage that no normal isotope strontium is added to milk. The strontium–90 and approximately twenty percent of the calcium and magnesium on the fixed-bed Dowex–50 resin is removed with a 5 molar sodium chloride solution delivered from tank **522** through lines **524**, **526**. The sodium-form resin is then reconditioned with about 250 gallons of fresh salt solution from tank **528**, through lines **530**, **504**.

The strong sodium chloride solution and the eluted strontium–90 and a small amount of calcium and magnesium are passed through line **532** to precipitation tank **534**. Sufficient sodium carbonate is added from tank **536** through line **538** to completely convert calcium and magnesium to the carbonate, and ferric chloride is added to form ferric hydroxide which aids in the scavenging. This precipitate will carry about 99% of the strontium–90. After filtration through filter **540** approximately 30–50 gallons of filter cake is obtained which may be removed for burial. The filtrate is largely strong sodium chloride solution, quite free from strontium–90, which may be recycled via lines **542**, **544** to tank **522** for the next regeneration of column **506**. In order to avoid dilution, a portion of this is thrown away (approximately 20%), and new sodium chloride is added.

DESCRIPTION OF THE ANION EXCHANGE COLUMN OPERATION

Because of the very favorable distribution coefficients for iodine–131 removal, it is possible to use a fixed-bed ion exchange resin column as shown in FIGURE 1, with the pH of the milk restored from its acidified level by the operation of the electrolytic cell **14**. However, it is preferred to use the continuous anion exchange resin column **340**, because of the lowered overall equipment costs.

Anion exchange column **340** is operated in a manner analogous to column **24** so far as valve manipulation, etc., is concerned. It is designed to accomplish neutralization of the original added acid by neutralization of hydrogen ions, and removal of iodine–131 falls within these conditions. As shown in FIGURE 2, the decontaminating section **342** may be of lesser volume than decontaminating section **28**, because of the faster exchange rate for the ion exchange resin for neutralization of hydrogen ions (and removal of iodine–131); thus, a smaller quantity of resin is required for a given volume of milk. In practice, it has been found satisfactory to have an anion decontaminating section volume of about two-thirds that used for the cation exchange decontaminating section.

With this arrangement, the milk flow volume rates through the two columns in the system illustrated in FIGURE 2 may be comparable, and essentially continuous milk flow achieved. This arrangement for constant throughput of the milk in both columns is also important to avoid any need for hold-up or waiting periods with the milk being processed. As already mentioned, unless the raw milk is held to a temperature of about 38° F–40° F., its bacteria count will go up quite rapidly.

During the operation of column **340**, the anion exchange resin is loaded with hydroxyl anion in section **366**, and, in section **342**, selectively adsorbs the chloride, and iodide, ions while neutralizing the acid with the hydroxyl ions.

Accurate control over the degree of exchange taking place in decontaminating section **342** is possible through pH sensing cell **346** and the pH servo-system **394** through driving pump **402**. This is, if the pH of the milk delivered through pipe **348** is the same as that originally supplied through pipe **340**, then due to the characteristics of the anion exchange loop **340**, and the selective exchange system, it is clear then that only the same amount of anions have been removed. Any excess exchange would, of course, be reflected in too high pH.

Any change in chloride content of the milk would indicate other anions are being exchanged, but the chloride content has been observed to be quite constant. The hydroxyl ion added to the milk in section **342** is, in fact, equal to the chloride and the iodine–131 ion content removed. In molar quantities, however, the iodine–131 content of the milk is extremely small, and, consequently, restoring the original pH of the milk removed effectively the same amount of chloride ions that has been added as hydrochloric acid.

Especially when using a weak-base resin, it is important to use hydrochloric acid to acidify the milk, as other acid anions do not exhibit this selective exchange of the anion with the ion exchange resin. For instance, the phosphate acids are apparently not sufficiently ionized, and the citric acids are generally too weak to permit this operation. Furthermore, because of the selective exchange in column **340**, it has been found unnecessary to regenerate this ion exchange resin with a balanced salt regenerate.

It is not practical to adjust the pH of the milk with an anion exchange resin in this manner with a fixed bed system because of batchwise-type pH formations in the milk, because the exchange rate varies so much from top to bottom in the fixed bed during operation and as it becomes loaded. Tests produced pH ranges fluctuating between 5.5 and 7.5 when fixed beds were used, even with rapid regeneration cycles.

It will be appreciated that the use of the strong hydrochloric mineral acid in this system is generally contrary to past practice in which strong acids were avoided because of more difficult mixing conditions and the danger of the precipitated milk protein resulting from localized high acid contents. Citric acid was employed because edible and a weaker acid. Agitation of the milk in the system of the present invention coupled with the exchange operation of column **340** permits the use of hydrochloric acid in a practical and effective manner.

For the anion exchange resin, two types may be employed, either a strong base type or a weak base type.

The weak base anion exchange resin has the advantage that the iodine–131 can be eluted with the sodium hydroxide regenerating solution, and this resin's inherent buffering effect was initially thought to have less possibility of causing undesirable fluctuations in milk pH. However, only about one-third of the iodine–131 is readily removed.

It has also been found possible to use strong base styrene type resins such as Dowex–2, X8, for these exhibit a very strong affinity for iodine–131. When these resins are used, it is actually very difficult to remove or elute the iodine–131 with the sodium hydroxide regenerate solution. While this would normally be considered a disadvantage, in this particular system, operation is possible

wherein the iodine–131 is never removed from the resin. With an eight-day half-life, the maximum build-up of radioactive iodide ion that can be established on the resin is an eight-day accumulation.

In experiments to determine the feasibility of this rather radical procedure, the sample of the strong base anion exchange resin was loaded very heavily with iodine–131, while above background readings. On contacting this resin in the usual way with milk at a milk-to-resin volume ratio of about 10 to 1, it was still found that at least 76% and perhaps as much as 95% of the iodine–131 contact would be removed at a steady state operation. These figures are conducted with induced iodine–131 concentrations in the milk approximately several million fold larger than the maximum concentrations so far observed.

Regeneration of the anion exchange resin, is achieved in section 366 with sodium hydroxide strip solution which may be supplied, as shown from reservoir tank 398. Only a very low volume of strip solution is required in practice, and this regenerating solution may be discarded without seriously affecting the economies of the system.

Caustic solution of one-fourth molar sodium hydroxide is introduced through line 364 for this regeneration, and pump 402 may be a dual-head positive displacement diaphragm type pump mixing 12 molar sodium hydroxide from tank 398 with 48 volumes of water. The flow through line 364 is adjusted to regenerate about 40% of the resin capacity to the hydroxide form by selectively displacing the chloride ions, iodine–131 being in no way affected by the hydroxide regenerant solution.

It has been found that so long as the iodine remains on the resin in iodide form it is not picked up by the milk but, if it is oxidized to elemental iodine, it can be removed, possibly by adsorption or complex formation with the casein or protein content of the milk. To prevent this, care should be taken to preserve a non-oxidizing environment for the resin. This may be done by using SO_2/water for cleaning a resin of the apparatus (instead of the more conventional chlorine water), and small amounts of sodium sulfate may be added to the hydroxide regenerating solution. Similar reducing agents could also be used.

DESCRIPTION OF DISTRIBUTOR MEANS ILLUSTRATED IN FIGURE 3

FIGURE 3 illustrates in greater detail the distributor means which are employed to introduce and remove the milk in the ion exchange column loops.

As shown in this figure, in section, the ion exchange column 24 (which, it will be understood, may also be column 340) is provided with mounting member 450 having a circumferential flange 452, suitably tapped to receive fastening bolts 454 at spaced points about the circumference of the flange. Mounting member 450 has a central bore 456 in alignment with a matching orifice 458 in the wall 460 of column 24. The bore 456 is generally conically enlarged outwardly from the juncture with wall 460, as shown at 462.

Disposed within and sealingly engaging the bore 456 of mounting 450 is the distributor member 464. As shown, the outer diameter of this distributor 464 is made just sufficiently smaller than the bore 456 of mounting member 450 as to permit sliding insertion of the distributor member 464 into the interior of column 24. Complementing the configuration of the interior of mounting member 450, the exterior profile of distributor 464 likewise conically enlarges exteriorally of the bore 460, with a taper substantially matching that of taper 462, as shown at 466. Application of a suitable grease, e.g. a silicone grease, on the surface of tapers 462 and 466 provides an adequate liquid-tight sealing engagement of the distributor to the mounting member 450. This is further secured by the tightening of fastening bolts 454 forcing the surfaces of tapers 462 and 466 tightly against each other, the flange member 468 on distributor 464 pressing against and engaging a gasket member 470.

The outer end of distributor 464 is further provided with the standard coupling member 472 for engaging the conventional milk union couplings now used in the dairy industry. When so connected, the interior bore 474 communicates with the milk supply, and permits delivery of the same to the interior of column 24 through holes 476. It will be seen that the distributor pipe has a closed interior end, but the plurality of holes 476 permits even distribution of the milk across the horizontal section of the apparatus.

Depending upon whether the distributor pipe is employed as an inlet or as an outlet, a screen is disposed within or without the pipe, and about the holes 476. This is a stamped metal screen having a large number of small holes rather than the conventional woven screen, and, of course, blocks movement of solid particles, e.g. ion exchange resin beads, through holes 476.

In FIGURE 3, this arrangement is illustrated in which the screen 478, with holes 480, is arranged within distributor pipe 464; whereas, in distributor pipe 464*a* in the upper part of the drawing, the screen 478*a* is arranged on the outside of distributor pipe 464*a*. It will be understood, of course, that this arrangement is shown only for purposes of illustration. Referring to FIGURE 1, all the distributor heads at distributor 26 in decontaminating section 28 would be arranged with the screen as shown in connection with distributor 464 at FIGURE 4; whereas distributor 30 would be provided with both distributor heads arranged as shown with distributor pipe 464*a* in FIGURE 3.

DISCUSSION OF SPECIFIC EMBODIMENTS OF THE INVENTION

As a presently preferred and specific embodiment of the invention, and with reference to FIGURE 2 of the drawings herein, this system may be conveniently arranged for the decontamination of 100,000 pounds or 12,000 gallons of milk per six-hour period.

For this purpose, the diameter of decontaminating section 28 may be about twenty-four inches and about five feet long between distributors 26 and 30. Regenerating section 82 can then be constructed with a twelve-inch diameter, with the inlet and outlet for the circulating regenerating salt solution being about six feet apart. Conduit sections 54 and 56 may also be of twelve-inch diameter, and the washing section 83 of about three feet in length.

Using such an ion exchange column loop as just described, the column loop 340 would appropriately have an approximate diameter of twenty inches. With the distance of approximately three feet between the milk distributors in this section. For the arrangement in which the iodine–131 is simply left on the anion exchange resin to there decay, it is sufficient to have a distance of about four feet between the inlet and the outlet for the sodium hydroxide regenerating solution delivered from supply tank 348.

Milk feed tank is maintained at a temperature of about 38° F., and pump 308 is established for a pumping rate of about 1,950 gallons per hour, with tank 327 having a capacity of 650 gallons, providing a twenty-minute hold-up. It is suitable to have hydrochloric acid supply tank having a capacity of approximately 50 gallons, to supply 300 pounds of 10 molar hydrochloric acid with 3,000 gallons water mixed therewith, per six-hour period through line 132. The pumping rate for pump 320 will, under these conditions be approximately one gallon per minute, although this will be adjusted as described hereinabove in accordance with the pH control system 332.

In the operation of this system, conditions are adequately maintained for a removal of some 99% of the strontium–90 and removal in the range of between 85 to 95% of the iodine–131 (with a strong base resin). Milk flow is maintained for three minutes, with an interruption of about ten seconds for (a) shifting the cation resin at

a rate of 3.1 liters/minute or some five inches in twelve-inch diameter reservoir section **59**, (*b*) the anion resin some 15 liters/minute or some 8 to 9 inches in twenty-inch diameter reservoir **377**, and (*c*) for restoration of the liquid interfaces, as related in connection with FIGURES 5–8. This establishes an overall milk flow rate to cation resin volume movement rate of about 40:1, and a similar ratio for the anion resin of about 8:1. The anion exchange resin distribution coeffiicient for iodide is approximately two hundred and fifty volumes to one volume, well within the above rate for the hydroxide/chloride exchange.

With this system, it is satisfactory to maintain a pressure head at pump **308** of approximately 30 pounds per square inch, but this may vary within the range of about 15 to 30 pounds per square inch, to achieve the desired constant flow throughput.

During this operation, for a period of six hours, the make-up regenerating salt circulated from tank **84** will amount to approximately $CaCl_2$, 360 lbs.; $MgCl_2$, 41 lbs.; NaCl, 132 lbs.; and KCl, 290 lbs. Usually about 20% of the total recovered regenerating salt solution content is replaced from tank **350** during an operating period of six hours.

It will be appreciated that generally in the operation of this invention, the factors principally determining the size of the apparatus and the parameters of the manipulative steps will be the overall production capacity desired, the distribution coefficient of the strontium–90 cation between the milk and the cation exchange resin, and the ion exchange rate.

Generally, in a typical dairy, the capacity of the system should provide for a processing of at least about 50,000 pounds of milk in a six-hour period, and a unit for processing 100,000 to 150,000 pounds is preferred.

The distribution co-efficient generally observed between milk and the cation exchanger resin is about 50 to 1. It is, therefore, desired to maintain the ratio of the volume of milk flow to the volume of resin flow in the decontaminating section as close to the ratio of 50 to 1 as is feasible, having in mind equipment size and desired capacity. The higher this ratio is maintained, while securing sufficient efficient removal of strontium–90, the less resin that is required. It is advantageous to maintain the resin volume at a minimum, in order to reduce the requirements for the regenerating salt solution. At the same time, the lower the milk flow to resin flow ratio, the more complete will be the removal of strontium–90. In the practice of this invention, it is preferred to maintain this ratio at at least about 70% and preferably at about 85 to 95% of the distribution milk/resin co-efficient. In these ranges, adequate strontium-90 removal of the order of 90 to 95% can be obtained at practical flow rates.

The milk flow rate through the decontaminating section is also preferably maintained to provide a contact period of about two minutes, and within the range of between about 1 to 3 minutes, depending upon the percent removal of strontium–90 which is required. This contact or "hold-up" time in the resin bed is determined by the rate of exchange of strontium–90 from the milk for the cations in the resin, which is affected, in all probability, by the extent of the complex retention of strontium–90 in the protein components of the milk (which is as aforementioned, in turn, affected by the pH).

The distribution of reagent to resin, for the cation exchange resin regenerating system, for removal of strontium–90 from the latter, is about 3 to 1, perhaps vary in the range of from about 2.5 to perhaps 5 to 1. It is important here to secure complete removal of strontium–90 from the resin, and consequently the ratio of regenerating salt solution flow to resin flow in the regenerating section will be maintained in excess of the distribution coefficient, within the range of from about 110 to 140%, preferably at least about 120 to 125%, for economically practical operations.

The shape of the columns, whether long and narrow or short and wide is not a determinative factor in the operation of the system, and the volumes of the respective operating sections are essentially established from calculation in the distribution cofficient and, hence, the liquid flow to resin flow rate ratios and the rate of ion exchange.

It will be understood from the foregoing description that this invention is not limited to practice according to the specific embodiments illustrated and described herein, and that variations thereof can be made while not departing from the principles involved. This invention is, therefore, to be understood to be limited only by the spirit and scope of the following claims.

I claim:

1. A continuous process for the radioactive decontamination of milk consisting essentially of:

(1) acidifying successive portions of the contaminated milk to be processed to reduce its pH to a level between about 5 and 6;

(2) flowing a first portion of said milk into a cation decontaminating section of an ion exchange column loop having a shiftable cation exchange resin bed therein, to bring the same into contact with a first portion of the cation exchange resin therein, and exchanging strontium–90 cations for at least one cation selected from the class consisting of calcium, magnesium, sodium, and potassium; while,

(3) simultaneously treating a second portion of said cation exchange resin in a regenerating section of said ion exchange column loop, by flowing a regenerating salt solution therethrough,

said regenerating salt solution consisting essentially of a balanced aqueous solution of calcium, magnesium, sodium, and potassium chlorides;

(4) substantially simultaneously interrupting the flow of said milk and said regenerating salt solution;

(5) shifting the cation exchange resin bed in said ion exchange column loop from one section thereof to another contiguous section therein,

thereby replacing at least a portion of said resin in said decontaminating section with another portion of said resin previously regenerated in said regenerating section and displacing a portion of resin carrying the cations previously eliminated from the milk into said regenerating section for regeneration thereof;

(6) thereafter re-establishing the liquid content of said decontaminating section as consisting of milk, while maintaining said decontaminating section free from adulteration with any liquid components other than milk;

(7) thereafter simultaneously flowing a second portion of said acidified milk and a second portion of said regenerating salt solution through said decontaminating and regenerating salt section respectively pursuant to steps (2) and (3) above;

(8) and repeating the same cycle of steps (4)–(7) as long as desired;

(9) treating the successive portions of milk removed from said decontaminating section to decrease the hydrogen ion content thereof, whereby the original pH of the milk is substantially restored.

2. The process of claim 1, wherein

(10) successive portions of said milk removed from said decontaminating section are introduced into an anion decontamination section of a second ion exchange column loop having a shiftable anion exchange resin bed therein to bring the same into contact with a first portion of the anion exchange resin in hydroxyl form, and thereby neutralizing hydrogen ions in said milk to restore said original pH of the milk, while simultaneously removing iodide–131 ions from said milk; while,

(11) simultaneously treating a second portion of said anion exchange resin in a hydroxyl regeneration section of said second ion exchange loop by flowing a regenerating aqueous alkali solution therethrough;

(12) substantially simultaneously interrupting the flow of said milk and said regenerating alkali solution in said second column loop;

(13) shifting said anion exchange resin bed from one section of said second column loop to another contiguous section therein,

thereby replacing at least a portion of said resin in said decontaminating section with another portion of said resin previously regenerated in said regenerating section and displacing a portion of resin carrying the anions previously eliminated from the milk into said regenerating section for regeneration of the hydroxyl ion content of the resin;

(14) thereafter re-establishing the liquid content of said anion decontaminating section as consisting of milk;

(15) thereafter simultaneously flowing further successive portions of said milk and said aqueous alkali regenerating solution through said anion decontaminating and said hydroxyl regenerating section pursuant to steps (10) and (11) above; and,

(16) repeating the same cycle of steps (12) to (15) as long as desired, whereby milk is obtained substantially free from radioactive cations and anions and of normal pH level.

3. The process of claim 2, wherein the said flow of portions of milk through said cation decontaminating section in step (2) and through said anion decontaminating section in step (10), are both conducted during a first predetermined period of time, and said shifting of said ion exchange resin beds in steps (5) and (13) is carried out within a second predetermined period of time.

4. The process of claim 1, wherein the regenerating solution consists essentially of an aqueous solution of said salts of predetermined composition to charge said resin with said cations in relative proportions corresponding to the proportions of said cations normally occurring in milk, whereby during said step (2) the cation balance of said milk aqueous hydrochloric acid in amount sufficient to removal of radioactive cations.

5. The process of claim 1, wherein said step (1) for acidifying the milk comprises turbulently adding to said milk aqueous hydrochloric acid in amount sufficient to reduce the pH to the said level, and thereafter holding the acidified milk for a period of time sufficient to permit at least a substantial part of the strontium–90 cations to be freed from protein complex in the milk, prior to introducing said milk into said ion exchange column in said step (2).

6. The process of claim 1, wherein said step (1) comprises flowing the milk through an electrolytic cell while applying an electrode potential thereacross and permitting passage of basic metallic cations from said milk and permitting replacement of basic metallic cations in said milk by hydrogen ions; and said step (9) comprises flowing the decontaminated milk through an electrolytic cell while a potential is applied thereacross while permitting discharge of hydrogen ions at the cathode of said cell and reintroduction of basic metallic cations into the said milk.

7. The process of claim 1, further comprising the steps of treating said regenerating salt solution to remove the strontium–90 displaced from said cation exchange resin to permit recycling of the same, which steps comprise adding to the regenerating salt solution an aqueous salt solution of a mixture of strontium chloride and calcium sulfate sufficient to form a co-precipitate of said strontium–90 as insoluble sulfate, and maintaining the thus-formed mixture at a temperature between about 80 to 95° C. for about one hour; filtering the solution to remove the radioactive precipitate therefrom; and thereafter adding a mixture of chloride salts of magnesium, calcium, sodium, and potassium, to establish the desired concentration of said regenerating salt solution, and recycling said salt solution to said regenerating section for regeneration of further portions of said cation exchange resin in accordance with said step (3).

8. The process of claim 1, wherein said regenerating salt solution is treated to remove its strontium–90 content, which process comprises the steps of passing said regenerating salt solution through a cation exchange resin having a high affinity for strontium–90 and adding to the eluted decontaminated regenerating salt solution a sufficient amount of a mixture of calcium, magnesium, sodium, and potassium salts to re-establish the desired concentrtaion for said regenerating salt solution; thereafter removing the strontium–90 from said ion exchange column by exchange for sodium ions, and subsequently conditioning the sodium-formed cation exchange resin by eluting therethrough a salt solution of calcium, magnesium, sodium, and potassium chlorides, whereby said cation exchange resin is in condition for reuse to decontaminate a further portion of said regenerating salt solution

9. The process of claim 8, further comprising the steps of removing strontium–90 from the sodium ion solution eluted from said cation exchange resin, comprising the addition of sodium carbonate and ferric chloride salts thereto to co-precipitate strontium–90, and filtering the precipitate to remove the same from said sodium ion solution, whereby it may be reused to treat said cation exchange resin.

10. The process of claim 9, wherein said step (2) and said step (5) are conducted so that the ratio of milk flow to resin flow through said decontaminating section is at least about 70% of the milk/resin distribution coefficient; and the milk is in contact with said resin in said decontaminating section for a period of time betwen about 1 to 3 minutes.

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