

EX 1005

(19) Japanese Patent Office (JP)

(12) **Published Patent Gazette (A)**

(11) Japanese Patent Application Publication No.  
Japanese Unexamined Patent Application Publication  
Official Gazette No. **H 10 (1998) - 255861**  
(43) [Publication date] **9.25.1998**

|                            |                                       |            |
|----------------------------|---------------------------------------|------------|
| (51) Int. Cl. <sup>6</sup> | Identification code JPO reference No. | FI         |
| H01M 10/54                 |                                       | H01M 10/54 |
| B03B 7/00                  |                                       | B03B 7/00  |
| B09B 5/00                  | ZAB                                   | B09B 5/00  |
| C22B 7/00                  |                                       | C22B 7/00  |
|                            |                                       | C          |
|                            |                                       | ZABA       |

Examination Request: Not yet made; Number of Claims: 9 OL (Total 21 pages)

(21) **Application No.:** Patent Application No. **H 9 (1997) - 59530**

(22) **Application Date:** **3.13.1997**

(71) **Applicant:** 000003078

**Toshiba Corporation**  
**72 Horikawa-cho, Saiwai Ward, Kawasaki City,**  
**Kanagawa Prefecture, Japan**

(72) **Inventor:** Yoshiki Tomioka

**8 Shinsugita-cho, Isogo Ward, Yokohama City,**  
**Kanagawa Prefecture, Japan,**  
**Inside Toshiba Yokohama Office**

(72) **Inventor:** Tomiaki Furuya

**8 Shinsugita-cho, Isogo Ward, Yokohama City,**  
**Kanagawa Prefecture, Japan,**  
**Inside Toshiba Yokohama Office**

(72) **Inventor:** Kimihiro Tadauchi

**8 Shinsugita-cho, Isogo Ward, Yokohama City,**  
**Kanagawa Prefecture, Japan,**  
**Inside Toshiba Yokohama Office**

(74) **Agent:** Patent Attorney Saiichi Suyama

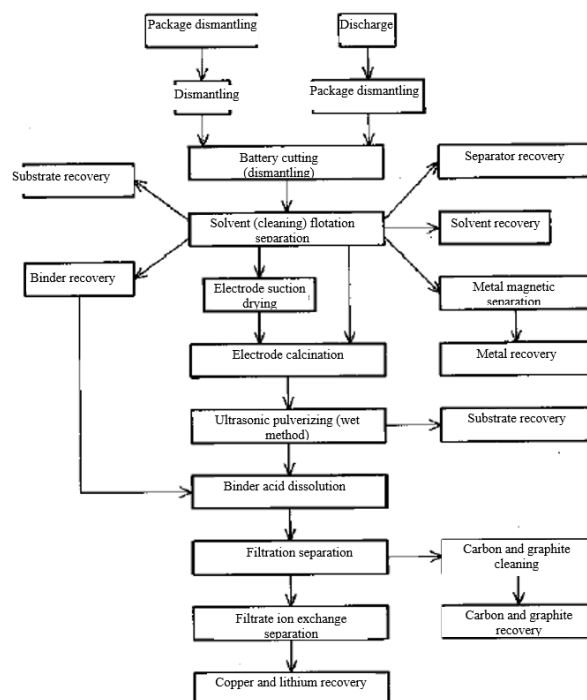
Continued on the last page.

**(54) [Title of Invention] Method for processing waste**

**(57) [Abstract]**

[Problem to be Solved] To provide a practical method for disposing of batteries that has high safety and low environmental impact.

[Means for Solving the Problem] The method for processing waste comprises the steps of dismantling the collected secondary batteries, cleaning the aforementioned dismantled battery components, heating the cleaned battery components, separating and crushing the active material layers in the electrode components of the heated battery components, immersing the powdered active material layer in an acidic solution to elute the soluble components, separating the insoluble components from the acidic solution, and precipitating and recovering the metal components in the acidic solution.



[Scope of Patent Claims]

[Claim 1] A method for processing waste, comprising a step of dismantling the collected battery, a step of cleaning the aforementioned dismantled parts, a step of heating the cleaned dismantled parts, a step of peeling and separating the active material layer of the electrode elements and crushing it, a step of soaking the powder of the active material layer in an acidic solution to elute soluble components, a step of separating the acidic solution from insoluble components, and a step of precipitating and recovering metal components from the acidic solution.

[Claim 2] A method for processing waste, comprising a step of discharging the collected battery, a step of dismantling the aforementioned discharged battery, a step of cleaning the dismantled parts, a step of heating the cleaned dismantled parts, a step of peeling and separating the active material layer of the electrode elements and crushing it, a step of soaking the powder of the active material layer in an acidic solution to elute soluble components, a step of separating the acidic solution from insoluble components, and a step of precipitating and recovering metal components from the acidic solution.

[Claim 3] The discharge processing step of the recovered battery as described in Claim 2, wherein the discharge processing step of the recovered battery is performed by connecting a conductor of the same material as the electrode collector to one of the battery electrode terminals via a conductive substance, and executing the discharge based on differences in ionization tendency.

[Claim 4] A method for processing waste as described in Claim 2, wherein the recovered battery is dismantled and soaked in an organic solvent selected from alcohol and ketones.

[Claim 5] A method for processing waste as described as described in Claim 1 or Claim 2, wherein the recovery of the battery is performed by passing a resin package enclosing the battery body through multiple rolls with differing rotational speeds to separate the resin package from the battery body.

[Claim 6] A method for processing waste as described as described in Claim 1 or Claim 2, wherein in the step of dismantling the recovered battery, the recovered battery is heated to vaporize and dissipate the internal liquid.

[Claim 7] A method for processing waste as described as described in Claim 1 or Claim 2, wherein in the step of dismantling the recovered battery, an opening is cut that is close to and approximately parallel to the sealing portion on the terminal protruding surface of the recovered battery, or an opening is cut at the corners where each surface intersects vertically.

[Claim 8] A method for processing waste as described in Claim 1 or Claim 2, wherein the dismantled electrode part is heated under a reducing atmosphere at a temperature below 600°C.

[Claim 9] A method for processing waste as described in Claim 1 or Claim 2, wherein the step of peeling and separating the active material layer of the electrode elements and crushing it is performed by placing it on a mesh of 10mm or smaller and applying vibration.

[Detailed Explanation of the Invention]

[0001]

[Technical Field to Which the Invention Belongs] This invention relates to a method for processing waste, particularly concerning methods or recycling techniques for used lithium-ion batteries and

nickel-metal hydride batteries.

[0002]

[Conventional Technology] In recent years, the demand for batteries for electronic devices such as laptops and mobile phones has dramatically increased. In particular, lithium-ion secondary batteries possess excellent characteristics, including high capacity per unit weight and volume and high voltage, making them an essential secondary battery for miniaturized electronic power sources.

Additionally, in California, where air pollution is becoming increasingly severe, a program to promote electric vehicle (EV) sales is expected to begin in 1998. Lithium-ion secondary batteries are being developed for use as these power sources, and a further surge in demand and consumption is anticipated. Consequently, the increase in battery consumption will inevitably lead to large-scale disposal (processing) of batteries, necessitating some form of waste treatment.

[0003] However, since lithium-ion secondary batteries and nickel-metal hydride secondary batteries have only recently been commercialized, practical methods for processing waste are still in a trial-and-error stage.

[0004]

[Problems to be Solved by the Invention] In the aforementioned lithium-ion secondary batteries, while lithium is stable in ionic form, it becomes highly reactive when metalized. Therefore, for safety reasons, it is desirable to centrally recover and dispose of lithium-ion secondary batteries through appropriate methods. That is, because lithium, which exhibits high reactivity when in metallic form, is used in lithium-ion secondary batteries, there is a significant risk of ignition and explosion. Furthermore, if disposed batteries are directly melted or decomposed in an incinerator, the internal pressure may increase, leading to a higher risk of explosion. From a resource perspective, it is also necessary to recover metals such as cobalt and nickel from the electrode elements. On the other hand, since harmful substances may be produced as by-products from fluorine and phosphorus contained in the electrolyte, there is a significant risk of environmental pollution, necessitating more appropriate disposal treatment.

[0005] Moreover, many small batteries, such as the aforementioned lithium-ion secondary batteries, may be used either as standalone units or in structures where multiple battery units are packed in a resin package. When the disposal item is a battery pack, it is crucial to first efficiently separate and remove the resin package so that the internal battery units can be extracted safely, enabling the recovery of useful resources. While one method to extract (separate) the battery units from the resin package involves manual disassembly at the junctions of the package, this approach is not suitable for large-scale disposal processing. Alternatively, mechanically crushing the disposal battery packs collectively, followed by wind separation and specific gravity sorting, could be considered as a mass processing method; however, there is also a risk of sparking due to residual voltage if the battery units are damaged in the process.

[0006] In addition, wiring boards are used in many fields, starting with high-performance electronic devices. These wiring boards are typically formed from materials such as valuable metals like copper foil and solder, inorganic substances like flame retardants, and resins, making waste disposal and recovery for reuse challenging.

Particularly when harmful substances are present, it is crucial to recover and neutralize these harmful substances without dispersing them while also addressing the difficulty of recovering valuable metals. This is significant both from an environmental perspective and in terms of resource utilization.

[0007] For the recycling of waste wiring boards, organic materials in the wiring board are removed through roasting, and gold from the copper foil and mounted components is recovered using a smelting furnace. This method can handle large quantities and is effective for recovering valuable metals; however, it poses problems from an environmental conservation and recycling standpoint. Specifically, there are concerns about the volatilization of harmful substances contained in the waste, such as lead compounds that have low melting points, and the generation of dioxins due to incomplete combustion. On the other hand, organic and inorganic materials are simply burned and discharged as slag, which has also been proposed for use as aggregate, but its value is lower compared to raw materials, limiting its applications.

[0008] To effectively recycle composite material products containing metals, inorganic materials, and organic substances, it is preferable to separate and sort each material without reducing their inherent energy potential. From the viewpoint of minimizing environmental impact, non-combustion separation technologies have been proposed. For instance, as a preprocessing step for separation, methods involving crushing and grinding the waste wiring boards followed by separation through specific gravity, static electricity, or eddy current sorting have been documented (e.g., Japanese Unexamined Patent Application Publication No. H 7 (1995) - 251154, Japanese Unexamined Patent Application Publication No. H 7 (1995) - 100436, etc.).

[0009] These separation techniques are effective in reducing environmental impact by suppressing the diffusion of harmful substances since they do not rely on combustion; however, because the separation depends solely on crushing, there are limitations to separation efficiency. Not only is the recovery rate of metals low, but a significant amount of metal contaminates the separated resins as impurities, which narrows down the possibilities for resin recycling and application.

[0010] This invention addresses the aforementioned circumstances and aims to provide a practical method for processing waste batteries that is safe and has low environmental impact.

[0011]

[Means for Solving the Problems] The invention of Claim 1 comprises a step of dismantling the collected batteries, a step of cleaning the dismantled parts, a step of heating the cleaned dismantled parts, a step of peeling and separating the active material layer of the electrode elements from the heated dismantled parts and crushing them, a step of immersing the powdered active material layer in an acidic solution to elute the acid-soluble components, a step of separating undissolved components from the acidic solution, and a step of precipitating and recovering metal components from the acidic solution.

[0012] Here, the collected batteries include, for example, individual

lithium-ion secondary batteries, lead-acid secondary batteries, battery packs (packaged batteries) containing circuit substrates, etc. Furthermore, "dismantling" means cutting the outer casing of the individual battery or the battery pack to extract the electrode element components such as the positive electrode, negative electrode, and separator, and if necessary, cutting them into strip-like pieces. The separation of the electrode element components may involve immersing them in a liquid (water, solvent, acidic, or alkaline liquid) after opening the casing of the battery, allowing them to separate by buoyancy, while concentrating and recovering electrolyte components like lithium hexafluorophosphate, ethylene carbonate, and dimethyl carbonate from the liquid used for immersion, and employing magnets to recover metal components floating in the aforesaid liquid.

[0013] Furthermore, the cleaning of the dismantled items can be performed using alcohols such as methyl alcohol or ethyl alcohol, ketones, or alcohol-water solutions. In this case, subsequent drying becomes easier, and peeling later is also facilitated. Additionally, if nitric acid is used as the cleaning solution, it allows for the separation of the substrate from the positive electrode and the binder, thereby eliminating the need for subsequent heating. On the other hand, when an alkali (for example, sodium hydroxide) is used as the cleaning solution, only the aluminum substrate of the positive electrode dissolves, making peeling unnecessary, and thus heating treatment can also be omitted.

[0014] In addition, following this cleaning process, to achieve the separation (decomposition) of the binder from the electrode elements and to remove any remaining solvents or binder components, a heat treatment is performed at a temperature of approximately 40 to 400°C. However, prior to this heat treatment, it is preferable to conduct a vacuum drying process to remove the electrolyte; this enhances the efficiency of subsequent processing.

[0015] Moreover, in this heat treatment, the temperature should be higher than that during electrode manufacturing (generally between 100 to 200°C), but below the temperature at which the fluorine in the binder of the electrode elements (PVdF: 400°C, fluorinated rubber: 300°C) volatilizes. By doing so, only the organic binder components are vaporized, suppressing the generation of harmful substances, while the difference in thermal expansion makes it easier to separate the electrode support and the active material layer.

[0016] Additionally, the peeling and separation of the active material layer from the heat-treated dismantled electrode elements can be preferably promoted by immersing the electrode elements in water and applying external forces, such as ultrasonic vibrations or blowing bubbles. The separation may also involve the decomposition and processing of wiring substrates that constitute part of the battery package. In such cases, it is desirable to structure the insulating substrate as a laminated structure with materials that impose different stress strains, making it easier to yield and cause internal failure under certain stress anomalies.

[0017] The acidic solution used to elute the acid-soluble components from the active material layer powder is intended to dissolve or ionize elements such as lithium, cobalt, and nickel within the

electrode elements. Generally, examples include hydrochloric acid solutions of 0.1 to 60% or nitric acid solutions of 0.1 to 60%. The separated undissolved components (organic components) are washed with water to remove the acid and collected, while the metal components in the aforementioned acidic solution are either separated and recovered by using ion exchange resins to adsorb (precipitate) the metals or precipitated and then separated and recovered.

[0018] The invention of Claim 2 is a method for processing waste that includes the steps of discharging the recovered battery, dismantling the aforementioned discharged battery, cleaning the aforementioned dismantled items, heat treating the aforementioned cleaned dismantled items, peeling and separating the active material layer of the electrode element of the aforementioned heat-treated dismantled items and grinding it, immersing the powder of the aforementioned active material layer in an acidic solution to elute acid-soluble components, separating the aforementioned acidic solution from insoluble components, and precipitating and recovering the metal components in the aforementioned acidic solution. The invention of Claim 3 is an improvement of the method for processing waste described in Claim 2, wherein the discharge process of the recovered battery involves connecting a conductor made of the same material as the electrode current collector to one of the battery electrode terminals via a conductive material, performing discharge based on differences in ionization tendency. This invention adds a step of performing a discharge treatment in advance to safely process the recovered battery for disposal. In other words, if a secondary battery in a charged state is dismantled directly, it could cause a short circuit and potentially ignite organic materials inside the battery; therefore, it is desirable to perform a discharge treatment beforehand. Possible means for this discharge treatment include the following:

[0019] ① For example, if carbon dioxide gas is generated inside the battery due to overcharging and the safety device has activated, cutting off the positive electrode lead, the external part of the battery can be cooled to about 0°C or compressed externally using a pump to liquefy the carbon dioxide gas inside the battery and restore the safety device.

[0020] ② Using a dedicated battery recovery box equipped with devices capable of executing the aforementioned method ①, the discharge treatment is performed during the transport process of the recovered battery or while the recovered battery is being stored.

[0021] ③ Immersing the recovered battery in an electrolyte similar to that in its electrode elements or a non-aqueous solvent to promote natural discharge of the battery. During this immersion, placing electrodes in the immersed electrolyte and connecting a resistor further promotes the discharge.

[0022] ④ If the recovered battery is in an overcharged state or an excessively discharged state, a conductor made of the same material as the electrode current collector is connected to one of the battery electrode terminals via a conductive material, and discharge occurs based on differences in ionization tendency. Here, the electrode current collector is preferably aluminum for the positive side and copper for the negative side, especially when there is a significant difference in ionization tendency.

[0023] For example, when observing the behavior of the negative electrode side connected to a metal immersed in another electrolyte under conditions where the positive and negative electrodes are not

short-circuited or the battery is not operating, we can see the following phenomena when lithium metal is either deposited on the negative side or not. In the state where lithium metal has deposited on the negative side (overcharged), metal present as ions in the electrolyte elutes from the metal immersed in the electrolyte, causing its weight to increase. Under constant voltage, the flowing electric current gradually decreases, and after some time, the deposition of the aforementioned metal almost stops, resulting in a sharp drop in the electric current value. This phenomenon indicates that, when comparing the standard electrode potentials of metals, the negative side of the secondary battery operates as one half-cell while the piece of metal immersed in the electrolyte acts as another half-cell, thus forming a new battery system.

In the case of an overcharged lithium-ion secondary battery, when lithium uniformly adheres around the copper foil current collector on the negative side, the standard electrode potential becomes lower than that of pure copper. As a result, the copper side connected to the metal immersed in the external electrolyte becomes the positive electrode, allowing electric current to flow. Moreover, the rapid change in electric current occurs because the lithium adhering to the negative side's copper foil current collector detaches, leading to resistance in electric current being dominated by the inherent resistance of copper. Therefore, with a certain voltage, the resistance value increases compared to when lithium was attached.

[0024] On the other hand, in the case of a secondary battery in an excessively discharged state, when forced to maintain a constant voltage under conditions similar to the aforementioned overcharge scenario, the metal immersed in the external electrolyte ionizes and acts as a negative electrode, making it easy to confirm the excessively discharged state.

[0025] The invention of Claim 4 is characterized by the method for processing waste described in Claim 2, wherein the recovered battery is dismantled and impregnated with organic solvents such as alcohols or ketones. The invention of Claim 5 stipulates that, in the method for processing waste described in Claim 1 or Claim 2, the recovered battery is one where the resin package enclosing the battery body is separated from the battery body by passing it through multiple rolls with differing rotational speeds.

[0026] This invention is characterized by how the recovered battery is separated from the resin package. Specifically, by passing a battery pack configured to enclose multiple batteries within a resin package through several rolls that have different rotational speeds, shear forces and twisting actions are simultaneously applied by the rotating rollers to break and peel off the resin package, thereby separating the enclosed battery body. The gap between the rolls must be set to be less than the overall thickness of the battery pack to ensure that sufficient force is transmitted to the resin package. At the same time, it must be set to be greater than the thickness of the battery body to avoid damaging it. Therefore, when applying this separation means, it is preferable to sort the battery packs by shape in advance. Moreover, if the batteries to be processed are mixed types with varying thicknesses and shapes, it is desirable to design the device configuration in advance to accommodate batteries of different thicknesses.

[0027] For example, one can establish multiple pairs of rolls with

varying gaps and utilize a sorting device located before the roll mechanism to either distribute the batteries to the processing rolls or direct them to a section where the gap between the rolls is gradually widened from one end to the other. The sorting method is not particularly limited as long as it sorts the recovered batteries by thickness; for instance, mechanical sorting can use multiple slits with varying widths, electromagnetic properties such as eddy current or electromagnetic induction can be applied for sorting, and shape recognition technology can use sensors like infrared or image processing methods. Commonly known methods can be employed.

[0028] The introduction of waste batteries into the roll apparatus is not particularly restricted as long as it is directed according to the settings of the roll gap. Generally, it is preferable to install a rectifying plate at the inlet so that the standardized direction by thickness does not get interchanged. In this case, to make it difficult for the introduction direction to interchange, it is most preferable that the batteries introduced into the roll gap match the thinnest direction of the battery thickness. Furthermore, it is preferable that this thinnest thickness direction is oriented perpendicular to the horizontal plane during introduction. Therefore, if there is a need to detect thickness, it is advisable to provide a means to adjust the most slender thickness direction to be perpendicular to the horizontal plane in front of the thickness detection means. This directional adjustment can be achieved, for example, by passing it over a vibrating flat plate.

[0029] Furthermore, the shear force and twisting action applied between the rolls during crushing and separation can be made even more powerful by using rolls with uneven surfaces. However, in order to avoid damaging the battery body, these uneven features should be set to a thickness below that of the resin forming the package. The shape of the uneven surface is not particularly restricted as long as it can reliably transmit the force of the roll, but a shape with moderately sharp angles is preferred. In other words, if the unevenness is too gentle, force transmission will be insufficient and ineffective. Conversely, if the unevenness is excessively sharp, there is a risk that the stripped package resin may adhere to the uneven surface due to temperature conditions or the viscoelastic properties of the resin forming the package, preventing it from separating from the roll. Therefore, it is preferable to set the angle of the uneven surface according to the characteristics at the processing temperature conditions of the resin package (case) of the battery pack being processed.

[0030] In addition, the roll apparatus that applies the necessary shear force and twisting action to the aforementioned resin package is a so-called roll-type kneading device or roll-type crusher. The shear force is applied by providing a rotational speed difference between two rolls through which the battery pack passes. Here, the speed ratio between the low-speed roll and the high-speed roll is generally in the range of 1:2 to 1:20, but preferably in the range of 1:3 to 1:8. Moreover, since the force acting on the battery pack (resin battery package) is fundamentally determined by the speed ratio, the rotational speeds themselves can be set arbitrarily considering

processing efficiency. However, if the rotational speed is excessively high, the deformation applied to the battery body increases, leading to the risk of damage. Thus, it is generally preferable to set the low-speed roll in the range of 20 to 500 rpm. Furthermore, when separating the resin package while breaking it away from the battery body, preheating the resin package to at least its softening point allows for the resin package to separate without applying deformation stress to the battery body. The heating method is not particularly restricted, and known methods such as electric heaters or infrared heaters can be used. It is effective to integrate or attach heating elements within the rolls themselves so that only the parts in contact with the rolls can be softened through direct heat conduction.

[0031] In addition, since the resin forming the package may adhere to the roll surface, it may be beneficial to attach a scraping mechanism, such as a fixed scraper or a movable rotating brush, or apply a release agent to the roll surface to prevent adhesion due to softening or melting of the resin.

[0032] Furthermore, the resin package that has been separated through the roll step and the battery body are each separated and recovered through the separation step. Here, various known methods can be used as separation means. Examples include specific gravity separation utilizing differences in density, air separation, as well as magnetic separation, eddy current separation, and electromagnetic induction-based sorting, which apply various electromagnetic properties.

[0033] The function of the invention described in Claim 5 is to enable processing of mixed waste batteries of multiple types by incorporating a step for selecting waste batteries with different thickness shapes prior to roll processing. By softening during the heating step, the package resin can easily be separated through the roll step, and through the separation step, the battery body and package resin can be sorted and recovered.

[0034] The invention of Claim 6 relates to the method for processing waste described in Claim 1 or Claim 2, wherein in the dismantling step of the recovered batteries, the recovered batteries are heated, causing the liquid contained within the battery to vaporize and dissipate.

[0035] The invention of Claim 7 pertains to the method for processing waste as described in Claim 1 or Claim 2, wherein in the dismantling step of the recovered batteries, a cutting opening is made so as to be nearly parallel to the sealing part close to the terminal protruding surface of the recovered battery, or a cutting opening is made at the corners where each face intersects vertically.

[0036] These inventions facilitate the removal of flammable organic solvents used in the electrolyte solution that forms a part of the electrode element, such as ethylene carbonate, methyl ethyl carbonate, and  $\gamma$ -butyrolactone, thus making subsequent processing easier. The means for vaporizing and dissipating the internal liquid includes (a) releasing the safety valve equipped in the battery due to the increase in pressure within the battery caused by vaporization, (b) heating and vaporizing after releasing the safety valve for dissipation,

and (c) cutting or opening the external battery can, for example, into rings to extract the electrode element, followed by heating and vaporizing for dissipation if necessary. It is preferable to recover these dissipated organic solvents by some means rather than releasing them directly into the atmosphere.

[0037] In these inventions, it is preferable to conduct a pre-treatment, such as vacuum suction drying using oil rotary pumps with gas collection mechanisms, piston pumps, multi-stage steam ejectors, Roots pumps, etc., before vaporizing and dissipating the liquid inside the battery. Here, the liquid within the battery may include materials such as methyl ethyl carbonate, dimethyl carbonate, diethyl carbonate, and ethylene carbonate.

[0038] Moreover, the cutting openings of the recovered batteries in the invention of Claim 7 can either be made nearly parallel to the sealing part close to the terminal protruding surface (in the form of ring cuts) or at the cutting openings of corners where each face intersects vertically. In the case of rectangular batteries, the cutting openings at the corners may involve the joint corners between adjacent side walls or the joint corners between the top/bottom surfaces and the side walls. In addition, for cylindrical batteries, they may include joint corners between the top/bottom surfaces and the side walls or incisions along the side wall extending between the top and bottom surfaces.

[0039] The invention of Claim 8 pertains to the method for processing waste as described in Claim 1 or Claim 2, characterized by heating the recovered and dismantled electrode element under a reducing atmosphere at a temperature below 600°C.

[0040] In this invention, the heating temperature of the electrode element part extracted through dismantling is generally sufficient to be below approximately 300°C; however, it can also be set to a high temperature limit of about 500°C. At this time, washing the extracted electrode element part with water or a solvent can prevent the generation of harmful substances such as hydrofluoric acid and aniline. On the other hand, if the heating temperature is set above approximately 300°C, it may cause decomposition of resin binders within the electrode element part, making peeling and separation more likely, but the generation of hydrofluoric acid can lead to corrosion and degradation of the heating furnace and surrounding areas. Therefore, it is advisable to use a corrosion-resistant furnace equipped with an acidic gas treatment device. In either case, it is desirable to circulate inert gases, such as nitrogen gas, to control the oxidation state of the organic binder by volatilizing and exhausting it.

[0041] The invention of Claim 9 relates to the method for processing waste as described in Claim 1 or Claim 2, wherein the step of peeling and separating the active material layer of the electrode element part is performed on a mesh of 10mm or smaller and involves applying vibration.

[0042] This invention provides a means for more efficient disposal of battery waste, allowing for easy peeling and separation of the active material layer of the electrode element part, as well as grinding. If necessary, this can be conducted while being heated to above 200°C. In other words, heating treatment or chemical treatment makes it easier to extract components from the battery element part, peel, and

decompose. Furthermore, placing the material on a mesh (for example, a conveyor) that is 10mm or smaller in size and applying a vibration treatment with an amplitude of about 10mm and a maximum frequency of approximately 1000 times per second enables simultaneous separation and grinding. Additionally, during this vibration treatment, spraying water or a solvent at a pressure of about 10 kgf/cm<sup>2</sup> can help avoid clogging.

[0043]

[Embodiment of the Invention] Below, Embodiments will be explained with reference to Fig. 1 to Fig. 22.

[0044] Embodiment 1

Fig. 1 is a flowchart showing the steps of this embodiment. First, a lithium-ion secondary battery (recovered battery) pack is prepared as the target for waste processing. Next, the recovered battery pack is dismantled by a battery pack dismantling device, as illustrated in side view in Fig. 2. Specifically, the battery pack 2 supplied from the supply hopper 1 is conveyed to the battery rectifying means 4 via the first conveyor 3. The battery rectifying means 4 has an inclined vibrating plate surface 4a that slides against a rectifying plate 4b installed at the lower end (outlet). This arrangement forms a slit width that allows the thinnest thickness face of the battery pack to align almost horizontally. The rectified battery pack 2 is then transported by the second conveyor 5, during which it undergoes heating treatment using a heating device 6, such as an infrared heater, arranged adjacent to the second conveyor 5.

[0045] The battery pack 2 subjected to the aforementioned heating treatment is supplied between a pair of rollers consisting of a low-speed roll 7a and a high-speed roll 7b, where roll peeling treatment is performed. Here, the low-speed roll 7a and the high-speed roll 7b are made of special steel with a diameter of 229 mm and an effective length of 457 mm, with the outer circumferential surface of both rolls set to a value 2 mm smaller than the thickness of the battery. The rotation speeds are set to mm/second on the low-speed roll 7a side and mm/second on the high-speed roll 7b side, respectively. If the outer circumferential surfaces of both rolls 7a and 7b are textured, they can be set to a value 2 mm greater than the thickness of the battery.

[0046] Through the aforementioned roll peeling process, the package of the battery pack is selectively destroyed and separated, while fragments remaining on the outer peripheral surfaces of both rolls 7a and 7b are removed by adjacent rotating brushes 8a and 8b, thereby being detached from the outer peripheral surfaces of both rolls 7a and 7b. On the other hand, the separated battery body 2a and package member 2b are separated by an air classification blower 9 into battery body 2a and package member 2b, and are housed in collection containers 10a and 10b, respectively.

[0047] Next, as shown in the cross-section in Fig. 3, the separated battery body 2a was housed and arranged within a glove box filled with argon gas, and placed into a wide-mouth bottle 11a made of tetrafluoroethylene resin, which contains 30 ml of electrolyte of the same type as that contained in the battery body 2a and has a capacity of 50 ml, for discharge processing. Moreover, in this discharge processing, the lid 11b of the wide-mouth bottle 11a is equipped with

a vent hole 11d with an inner diameter of 5 mm, which includes a safety valve 11c that opens when the internal pressure rises. After sealing with the lid 11b and leaving it in the glove box for two weeks, it was found that the battery voltage, initially about 3.6V, had decreased to 0.6V.

[0048] The discharged battery body 2a from the previous step is dismantled using a battery body disassembly device, as shown schematically in Fig. 4. Specifically, the battery body 2a is fixed to a rotating table 13 by a fixing claw 13a driven by a motor 12. The cutting position of the fixed battery body 2a is aligned with a cutting reference plane 14. While rotating the table 13, its rotation axis 13b is moved back and forth. Meanwhile, an insulated oil is injected from a high-pressure injection nozzle 15 set at a diameter of 0.35 mm and a stand-off distance of 2 mm, maintained at about 80°C, under a pressure of 3000 kfg/cm<sup>2</sup> to cut and open the terminal lead-out side of the battery body 2a almost horizontally, enabling the dismantling of the battery element part for removal. Moreover, in Fig. 4, 16 is a buffer tank for insulating oil, 17 is a high-pressure pump, 18 is an abrasive supply unit, 19 is a recovery tank, and 20 is piping equipped with an opening and closing valve 21.

[0049] Next, the battery element part is removed through the cutting/opening section of the battery body 2a and immersed in isopropyl alcohol for approximately 10 minutes of shaking cleaning. If necessary, it is then removed from the isopropyl alcohol and dried at 10<sup>-1</sup> Torr for 15 minutes using a Roots pump, ensuring that the surface is nearly completely dry. After this, as shown in cross-section in Fig. 5, heating treatment is performed for about one hour using a nitrogen gas recirculation electric furnace 22 preheated and adjusted to 250°C. Other extracted battery element parts (separator, solvent, precious metals) are separately collected.

[0050] A detailed explanation regarding the drying effect at 10<sup>-1</sup> Torr for 15 minutes using the Roots pump is provided. Specifically, the nitrogen gas recirculated during the heating drying process at 250°C in the nitrogen gas recirculation electric furnace 22 is collected in an alkaline aqueous solution, and the concentration of phosphorus and fluorine (mg/kg) is measured and detected using ion chromatography, resulting in the values shown in Table 1.

[0051]  
[Table 1]

|                          | Phosphorus<br>Amount | Fluorine<br>Amount |
|--------------------------|----------------------|--------------------|
| With Vacuum Drying       | <0.02                | <0.02              |
| Without Vacuum<br>Drying | <0.02                | 0.03               |
| Without Water<br>Washing | 2740                 | 3590               |

In addition, after shaking cleaning for approximately 10 minutes by immersing the extracted positive electrode in isopropyl alcohol and allowing it to dry naturally, the positive electrode was sent via a belt conveyor into an electric furnace set at a temperature of 150°C for one hour of heating treatment, or alternatively sent into an electric furnace set at a temperature of 400°C for one hour of heating treatment. The results of measuring the 180° peel strength (g/mm) of

the positive electrode are shown in Table 2. As can be seen from Table 2, heating at 400°C effectively peels off the supporting substrate and active material (binder) layer of the electrode.

[0052]  
[Table 2]

|                | 180° Peel Strength |
|----------------|--------------------|
| Natural Drying | 19                 |
| 150°C Heating  | 18                 |
| 400°C Heating  | 0                  |

The supporting substrates and binders of the heated positive and negative electrodes are separated, peeled off, and recovered as follows: First, a reaction tank 24 is prepared, as shown in a cross-sectional view of the structure in Fig. 6. This tank includes a gas diffusion tank 24a for diffusing gas pressed in by a gas inflow pump 23, and a bubble diffusion plate 24b for diffusing solvent injected by a solvent injection pump 25. An ultrasonic generator 26 is positioned around the outer perimeter of the reaction tank 24, along with a rotating screen 27, a solvent circulation reservoir 28, and a stirring tank 29 for the separation and recovery equipment. Moreover, in Fig. 6, 30 is the gas inflow valve, 31 is the circulation valve, 32 is the three-way valve, and 33 is the stirrer.

[0053] Next, the reaction tank 24 is set up in such a way that air rises in bubbles at a rate of approximately 20 liters per minute while swirling in the water contained within the aforesaid reaction tank 24. Within this reaction tank 24, electrode fragments that have been pre-crushed to about 10 mm or less are housed. At this time, ultrasound with a frequency of 15,000 Hz to 50,000 Hz is emitted by an ultrasonic generator 26, providing fine vibrations, while the bubbles are also controlled to ensure that the electrode fragments remain suspended in the water of the reaction tank 24 for a certain period of time. During this processing stage, the electrode fragments separate into support substrates, binder-based particles, and collector layers. While the collector layers are screen-trapped, the particulate matter is allowed to flow out of the reaction tank 24, with water being directed to a solvent circulation storage tank 28 and the water containing binder-based particles being separated and collected into a stirring tank 29.

[0054] The aforementioned recovered particulate material is refined and recovered according to the procedure shown in the flowchart in Fig. 7. For example, in the case of binder-based positive electrode particles, they are placed in a polyethylene container, hydrochloric acid at a concentration of about 6% is added, and the mixture is heated to about 80°C to dissolve lithium cobalt oxide, allowing insoluble components to be filtered and separated. After that, the liquid filtrate from which the insoluble components have been filtered out is transferred to, for instance, a polyethylene beaker, to which 1500 ml of distilled water and 50 ml of hydrofluoric acid are added. This solution is then passed through a polyethylene column filled with 10 ml of cation exchange resin (100~200 mesh). After the liquid filtrate passes through the column, the operation of flowing 10 ml of 1% hydrofluoric acid through the column is repeated three times, followed by repeating the operation of flowing 10 ml of 0.2% hydrochloric acid three times. Furthermore, the operation of flowing 10 ml of 8% hydrochloric acid is repeated four times to elute cobalt ions from the column. After this, 2 ml of 18% sulfuric acid is added to the eluted cobalt ion solution, which is then heated to 120°C to

evaporate the solvent, followed by heating in air at 1000°C for about one hour to recover cobalt oxide. The weight of the obtained cobalt oxide was measured, and the recovery rate of cobalt was calculated to be 98%. Moreover, the aforementioned electrode peeling after washing can be performed using the following methods. First, as a first method, as schematically shown in Fig. 8, an electric furnace 22 equipped with a control unit 22a is heated and conveyed at a temperature set to 230°C for a retention time of one hour. It is sent onto a U-shaped stainless steel belt conveyor 34 with a mesh size of 5 mm, which belt conveyor 34 is vibrated up and down at an amplitude of 50 mm and a frequency of 2/sec. After 20 minutes of vibration treatment, pure water is sprayed in a shower-like manner at a flow rate of 7.28 ml/min, leaving the supporting substrate on the mesh while washing away the crushed electrode binder, thus peeling and separating the two. Upon observing the residual supporting substrate with an electron microscope, it was confirmed that only an average of 0.4% of the electrode binder remained per unit area, indicating that separation was nearly complete.

[0055] The second method, as schematically shown in Fig. 9, involves preparing an electric furnace 22 that contains a stainless-steel dish 35 with a 10 mm mesh inside and has a mechanism that can impart vibration with an amplitude of 18 cm and a frequency of 0.5/sec through the action of a piston 36. In the mesh dish 35 of electric furnace 22, about 50 g of electrode pieces cut into strips after washing are placed, sealed with a lid 37 (maintaining a distance of 20 cm from the upper edge of the mesh dish 35), and the temperature of the electric furnace 22 is set to 300°C for the separation treatment. In this separation treatment, the electrode binder, which has become easier to peel off due to the decomposition of the binder, falls from the mesh dish 35 below and separates easily from the supporting substrate. The electrode binder that fell from the mesh dish 35 is taken out from the lower outlet 22b and dissolved in hydrochloric acid for quantitative analysis using ICP-AES, recovering 8 g of cobalt.

[0056] In the aforementioned case, since the battery package was used as a material for recovery and processing, the dismantling of the battery package was conducted first. However, when recovering and processing the secondary battery body (the battery itself), the step of dismantling the battery package is omitted. In addition, if the secondary battery being recovered and processed is already in a discharged state, the discharge processing step is also omitted.

[0057] Embodiment 2

This embodiment is characterized by the discharge processing step of the recovered battery in the aforementioned Embodiment 1.

Specifically, a conductor made of the same material as the electrode collector is connected to one electrode terminal through a conductive material, and discharge is performed due to differences in ionization tendency. By detecting changes in this discharge electric current, it resolves the overcharge state.

[0058] In other words, focusing on the electrochemical properties related to the presence or absence of lithium metal deposited on the negative electrode side, while keeping the positive and negative electrodes of the battery in a non-short-circuited and unused state, the negative electrode side is connected to a metal (for example, copper) immersed in another electrolyte, and the behavior at that time is observed. When lithium metal is deposited on the negative electrode

side, the metal immersed in the electrolyte deposits ions from the electrolyte, resulting in an increase in weight, and the electric current flowing under a certain voltage gradually decreases. After some time has passed, the electric current value sharply decreases, at which point the deposition of metal onto the metal immersed in the aforementioned electrolyte also nearly stops.

[0059] This phenomenon can be explained by comparing the metals at standard electrode potentials. In this case, when the negative side of a secondary battery is treated as a half-cell, it is connected externally, and the metal immersed in the electrolyte functions as the other half-cell, forming a single battery system.

[0060] Here, in an overcharged lithium secondary battery, if lithium adheres uniformly around the copper foil that forms the collector, the standard electrode potential drops below that of pure copper. Consequently, the metal immersed in the electrolyte (copper) becomes the positive electrode, while the copper of the lithium second battery, which has lithium adhered to it, becomes the negative electrode, allowing electric current to flow. The abrupt change in electric current occurs because lithium leaves the copper electrode as ions, resulting in the resistance of the current path being dominated by the intrinsic resistance of copper, leading to a higher resistance value than when lithium was adhered.

[0061] Therefore, the time until the electric current changes significantly, the degree of change in electric current values, and the electric current values themselves can reveal the overcharge state of the recovered secondary battery. This involves confirming changes in the aforementioned electric current and converting lithium metal to lithium ions.

[0062] On the other hand, detection of the overcharge state can be accomplished by knowing the size and rating of the secondary battery, thereby determining the copper content per secondary battery. By connecting the negative electrode side to a metal (copper) immersed in another electrolyte and monitoring the weight change of that metal plate or changes in electric current values, rough proportions of the copper that has been ionized due to overcharging can be identified. Additionally, when detecting the overcharge state, a controlled constant voltage is applied, establishing a configuration where the metal immersed in the electrolyte becomes the negative electrode.

[0063] In this embodiment, the lithium-ion secondary battery (recovered battery) pack intended for disposal is dismantled following the procedure outlined in the aforementioned Embodiment 1. Specifically, a battery pack dismantling device, which shows a schematic configuration from a side view as illustrated in Fig. 2, is used. The battery pack supplied from supply hopper 1 is sent to the battery rectifying means 4 via first conveyor 3. The battery pack slides along the inclined vibrating surface 4a of the battery rectifying means 4, and by the slit width formed with the rectifying plate 4b installed at the lower end (outlet), the thinnest thickness surface is rectified to face approximately horizontally. The rectified battery pack 2 is then conveyed by second conveyor 5, during which heating treatment is applied using a heating device 6, such as an infrared heater, positioned adjacent to the second conveyor 5.

[0064] The battery pack 2 subjected to the aforementioned heating treatment is supplied between a pair of rollers composed of a low-speed roll 7a and a high-speed roll 7b, where a roll peeling process is performed.

[0065] As a result of the aforementioned roll peeling process, the

package of the battery pack is selectively destroyed and separated, detaching from the outer circumferential surfaces of both rolls 7a and 7b. On the other hand, the separated battery body 2a and package member 2b are separated by an air classification blower 9 into battery body 2a and package member 2b, and are housed in collection containers 10a and 10b, respectively. Next, using a means as schematically illustrated in Fig. 10, the charge state of the recovered batteries is detected. In Fig. 10, 38 represents a rectangular lithium secondary battery with a nominal voltage of 3.6V (thickness 8.6mm, width 34mm, length 48mm), which has metal precipitated on the negative electrode side as observed through X-ray imaging. Here, the secondary battery 38 has a configuration where a negative electrode 38b, separator 38c, positive electrode 38d, and electrolyte 38e are housed within an outer can 38a, and it is hermetically sealed. The aforementioned electrolyte 38e contains lithium ions 38f, carbon 38g, metals (Co, Mn, Ni) 38h, oxygen 38i, and so forth. On the other hand, an external setup is prepared consisting of a container 39 that houses an electrolyte (for example, a 1 mol/l copper sulfate solution) 38e', and a metal copper piece (for example, a rolled copper foil of thickness 0.01mm, width 4cm, length 40cm) 40 soaked in the aforementioned electrolyte 38e'. This is electrically connected to the negative electrode 38b of the secondary battery 38 via a DC power supply 41 and an electric current meter 42.

[0066] In this state, a voltage of 2.5V is applied from the DC power supply 41, and when the electric current value at that time was read, as shown in Fig. 11, it was confirmed that after a certain period, the electric current value decreased sharply and converged. After stopping the voltage application from the aforementioned DC power supply 41 and removing the metal copper piece 40 soaked in the electrolyte 38e', an 8% weight increase was observed. At this point, the secondary battery 38 was again subjected to X-ray imaging to observe the negative electrode side, where no unwanted metal deposits were noted, and there were no incidents of ignition even during discharge processing.

[0067] Furthermore, when a rectangular lithium secondary battery with a nominal voltage of 3.6V was processed under the same conditions as aforementioned, the amount of metal precipitated on the negative electrode side detected by X-ray imaging showed a similar phenomenon, with a weight increase of 16% for the metal copper piece 40 soaked in the electrolyte 38e'. On the other hand, when a similarly discharged rectangular lithium secondary battery was processed, since the electric current value was low from the start, the polarity was reversed, but it still maintained a high electric current value. After matching the voltage application time with that of the aforementioned case and measuring the concentration of the electrolyte 38e', it was found to be a 10% increase. In addition, at this point, the battery interior was again observed through X-ray imaging, revealing an increase in the metal copper portion.

[0068] The detection of the charge state of the aforementioned recovered batteries may also be conducted as follows. That is, as schematically shown in Fig. 12, using external equipment comprising a container 39 that houses the electrolyte (for example, a 1 mol/l copper sulfate solution) 38e', and multiple metal copper pieces (for example, rolled copper foil pieces of thickness 0.01mm, width 4cm, length 40cm) 40 arranged at approximately 2mm intervals, it can also be performed. Moreover, the same parts as in Fig. 10 are indicated with the same symbols.

[0069] In this case as well, a voltage of 2.5V was applied from the DC power supply 41, and upon reading the electric current value at that time, it was confirmed that after a certain period, the electric current value decreased sharply and converged, as shown in Fig. 13. After stopping the voltage application from the aforementioned DC power supply 41 and removing the metal copper piece 40 soaked in the electrolyte 38e', an 8% weight increase was observed. At this point, the secondary battery 38 was again subjected to X-ray imaging to observe the negative electrode side, where no unwanted metal deposits were noted, and there were no incidents of ignition even during discharge processing.

[0070] On the other hand, when similar treatment was performed on a lithium secondary battery in a discharged state, the electric current value was low from the beginning, so the polarity was reversed, but it still maintained a high electric current value. After matching the voltage application time with that of the aforementioned case, the concentration of the electrolyte 38e' was measured, resulting in a 4% increase. In addition, at this point, the battery interior was again observed through X-ray imaging, revealing an increase in the metal copper portion.

[0071] Furthermore, in the embodiment shown in Fig. 14, the top cover (sealing lid) of the lithium secondary battery 38 was removed and opened, and filled with a solvent such as ethylene carbonate. The metal copper piece 40 soaked in the electrolyte 38e' was connected to a salt bridge 43 filled with potassium chloride gel, and the detection of the charging state was conducted under similar conditions. In Fig. 14, the same parts as in Fig. 10 are indicated with the same symbols.

[0072] In this case as well, a voltage of 2.5V was applied from the DC power supply 41, and upon reading the electric current value at that time, it was confirmed that after a certain period, the electric current value decreased sharply and converged, as shown in Fig. 15. After stopping the voltage application from the aforementioned DC power supply 41 and removing the metal copper piece 40 soaked in the electrolyte 38e', an 8% weight increase was observed. At this point, the secondary battery 38 was again subjected to X-ray imaging to observe the negative electrode side, where no unwanted metal deposits were noted, and there were no incidents of ignition even during discharge processing.

[0073] On the other hand, when similar treatment was performed on a lithium secondary battery in a discharged state, the electric current value was low from the beginning; thus, the polarity was reversed, but it still maintained a high electric current value. After matching the voltage application time with that of the aforementioned case, the concentration of the electrolyte 38e' was measured, resulting in an 8% increase. Additionally, at this point, the battery interior was again observed through X-ray imaging, revealing an increase in the metal copper portion.

[0074] In this way, after confirming the charging state of the recovered battery, the process is conducted in accordance with Embodiment 1. The recovered battery is housed and arranged within a glove box filled with argon gas and placed into a wide-mouth bottle 11a made of tetrafluoroethylene resin, which contains an electrolyte of the same type as that of the recovered battery, for discharge processing.

[0075] The discharged recovered battery was then decomposed using the battery main body disassembly apparatus illustrated in Fig. 4. Next, the battery element was retrieved through the cutting/opening part of the recovered battery, and the positive and negative electrodes

were immersed in water for approximately 10 minutes of shaking and cleaning. If necessary, the electrodes were taken out of the water and vacuum-dried at  $10^{-1}$  Torr using a Roots pump, ensuring that the surface was nearly completely dry before conducting heating treatment in a nitrogen gas reflux-type electric furnace preheated and adjusted to 250°C. After that, other components of the battery (separator, solvent, precious metals) were separately recovered, and by methods such as flotation, the electrode binder components and support substrates were separated and each processed for recovery.

#### [0076] Embodiment 3

This embodiment pertains to a method for processing waste that significantly reduces or eliminates risks associated with the treatment of recovered batteries through discharge processing, as described in the series of steps outlined in the aforementioned Embodiment 1.

[0077] Fig. 16 shows a discharge processing device suitable for the discharge treatment during the disassembly processing of recovered batteries. Here, 44 is a double-structured cooling outer container made of stainless steel, 44a is its lid, and 45 is a stainless-steel double-structured cooling inner container that contains a circuit including a resistor (for example, approximately 10Ω) 46 and can accommodate the recovered battery 47. 45a is the lid of the cooling inner container, 48 is a cylinder containing liquid nitrogen for cooling, 49 is the liquid nitrogen injection and control valve, and 50 is a heat insulation sheet that covers the aforementioned cooling outer container 44.

[0078] Next, an example of the discharge treatment will be explained. First, a lithium secondary battery that has undergone overcharging treatment resulting in the generation of carbon dioxide gas inside is prepared and placed inside the cooling container 45, where it is electrically connected and mounted to the internal circuit. Then, after sealing the lid 45a of the cooling inner container, liquid nitrogen is poured into the cooling outer container 44, the liquid nitrogen injection and control valve 49 is closed, and after sealing it with the lid 44a, it is wrapped with the heat insulation sheet 50 and left for one day to perform the discharge.

[0079] After the aforementioned waiting period, the heat insulation sheet 50 is removed, and once it is confirmed that the liquid nitrogen has vaporized, the cooling outer container 44 and the cooling inner container 45 are opened sequentially. Inside the cooling outer container 44, which has been filled and replaced with argon gas, both ends of the recovered battery 47 are cut using a ceramic cutter to disassemble the battery. In this battery disassembly process, neither heating nor ignition occurred, allowing the dismantling of the battery to be safely performed.

#### [0080]

In addition, instead of the aforementioned discharge treatment, it can also be carried out as schematically shown in Fig. 17. Specifically, a resin opening-and-closing box 51 containing a circuit with a resistor 46 is prepared, along with insulating springs 52a and 52b that secure the positive and negative sides of the recovered battery 47, and insulating sponges 53a and 53b that act to provide cushioning during the fixation of the recovered battery 47. On the other hand, a recovered battery 47 charged to 3.6V is prepared and mounted in the aforementioned gloved box for three days. After this period, when the recovered battery 47 is removed and the voltage is measured, it was confirmed to have dropped to a safe level of 0.5V for dismantling the battery. This discharge treatment method is advantageous due to its simplified structure, lightweight design, and portability, allowing for

discharge processing during transport. After the aforementioned discharge treatment, subsequent processes such as battery disassembly, cleaning, and separation were carried out similarly to those in Embodiment 1, enabling safe disposal of the battery.

[0081] Moreover, in the discharge processing when disassembling the recovered battery, a method may also be employed in which some external pressure is applied to the recovered battery. This external pressure temporarily separates the battery elements or electrical circuits, allowing for either natural or forced discharge.

#### [0082] Embodiment 4

This embodiment is characterized by a waste processing example where the resin package enclosing the battery body is peeled off and separated. The recovery of the battery is accomplished by passing it between multiple rolls that rotate at different speeds, thereby separating the resin package from the battery body. This process is carried out in accordance with the embodiment illustrated in the aforementioned Fig. 1.

[0083] As waste battery samples, a lithium-ion secondary battery pack packaged in a polycarbonate-butadiene-styrene copolymer resin (softening point 118°C) or a mixed system containing three types of lithium-ion secondary battery packs with different dimensions and shapes (dimensions: rectangular type 40×53×10 mm, cylindrical type 30×54×16 mm, rectangular type 69×173×19 mm) in equal numbers was prepared.

[0084] On the other hand, a roll peeling device equipped with a pair of rotary rolls made of special steel with a diameter of 229 mm and effective length of 457 mm, which have a rough surface with unevenness, was prepared. Here, the rotary rolls are set to have a rotation speed ratio of 1:3, and the gap between the outer surfaces of both rotary rolls is set to be 2 mm smaller than the thickness of the battery.

[0085] In the case of a single system of the aforementioned waste battery, it was rectified and supplied to the roll peeling separation device. Upon dismantling and separating the resin package from the battery body, only the resin package was destroyed, allowing for easy peeling from the battery body for manual sorting. In the case of the mixed system, after being rectified in parallel and separated into three types, they were each supplied to the roll peeling device with the outer surface spacing of the rotary rolls adjusted accordingly. The result of dismantling and separating the resin package from the battery body yielded a sorting yield of 90%. Furthermore, when the mixed waste battery was divided widthwise through parallel rectification into three types, and the outer surface spacing of the rotary rolls was changed accordingly for dismantling and separation, the sorting yield was 86%.

[0086] When performing the dismantling and separation (roll peeling) of the aforementioned battery package, variations were made in whether the disposal battery package was single or mixed, the presence or absence of preheating of the disposal battery package, the presence or absence of unevenness on the outer surface of the rotary rolls, and the rotation speed and speed ratio (rotation ratio) of the rotary rolls. The resulting sorting (manual sorting or air sorting) yields are shown in Table 3.

[Table 3]

| Sample | Recovered Battery | Preheating (°C) | Rotary Roll Conditions         |                |                |                | Post-roll Sorting | Sorting Yield (%) | Processing Speed (items/min) |
|--------|-------------------|-----------------|--------------------------------|----------------|----------------|----------------|-------------------|-------------------|------------------------------|
|        |                   |                 | Surface Unevenness of the Roll | Rotation Ratio | Rotation Ratio | Rotation Ratio |                   |                   |                              |
| a      | Single            | None            | None                           | None           | 60             | 1:3            | Manual sorting    | 98                | 40                           |
| b      | Single            | None            | None                           | None           | 60             | 1:3            | Air sorting       | 50                | 120                          |
| c      | Single            | None            | Yes                            | None           | 60             | 1:3            | Air sorting       | 70                | 120                          |
| d      | Single            | 130             | Yes                            | None           | 60             | 1:3            | Air sorting       | 90                | 120                          |
| e      | Single            | None            | Yes                            | 210            | 60             | 1:3            | Air sorting       | 92                | 120                          |
| f      | Single            | 90              | Yes                            | 180            | 60             | 1:3            | Air sorting       | 96                | 120                          |
| g      | Single            | 90              | Yes                            | 200            | 120            | 1:3            | Air sorting       | 90                | 240                          |
| h      | Single            | 90              | Yes                            | 180            | 60             | 1:6            | Air sorting       | 92                | 120                          |
| i      | Mixed             | 90              | Yes                            | 180            | 60             | 1:3            | Air sorting       | 90                | 90                           |
| j      | Mixed             | 90              | Yes                            | 180            | 60             | 1:3            | Air sorting       | 90                | 90                           |

By the aforementioned roll peeling process, the resin package of the battery package is selectively destroyed and separated. The fragments of the destroyed and separated materials that adhere to and remain on the outer surfaces of both rolls are removed by a rotating brush arranged adjacent to them. On the other hand, the separated battery body and packaging materials are sorted using an air classification blower or similar device, which separates them into the battery body and packaging materials, each being collected in designated containers.

[0087] In this way, the separated and recovered battery body undergoes steps including discharge processing, battery dismantling processing, cleaning of the dismantled battery components, heating treatment of the electrode elements, stripping of the active material layers, and processing/recovery of the stripped active material layers, similarly to what was described in the aforementioned Embodiment 1. This ensures effective waste processing with good productivity.

[0088] Embodiment 5

This embodiment aims to enhance the safety of the dismantling operation of recovered batteries by heating the batteries and pre-vaporizing or evaporating the internal liquids. For example, in the case of lithium secondary batteries, flammable solvents such as ethylene carbonate (boiling point 238°C), methyl ethyl carbonate (boiling point 127°C), and  $\gamma$ -butyrolactone (boiling point 204°C) containing fluorine or phosphorus are included as electrolytes. These flammable solvents may ignite due to short circuits between the positive and negative electrodes during the disassembly process or generate harmful gases such as hydrofluoric acid; thus, it is desirable to remove and recover them as much as possible.

[0089] And, the removal and recovery of the solvent that makes up the aforementioned electrolyte can be achieved through: (a) vaporizing the liquid inside the battery and utilizing the pressure increase to open the safety valve, (b) opening a portion of the battery through cutting and then vaporizing the liquid inside the battery to

allow it to evaporate, with the generated evaporated gas being cooled and condensed for recovery.

[0090] Fig. 18 schematically illustrates an example of one embodiment for the removal and recovery of the solvent constituting the electrolyte. In Fig. 18, 54 is the container body that houses the recovered battery 55, 54a is the lid, 56 is a heater for heating the aforementioned container body 54, 57 is a temperature measuring device for measuring and detecting the temperature inside the container body 54, 58 is a controller that controls and adjusts the heating by heater 56 based on the information from the aforementioned temperature measuring device 57, 59 is a condenser that cools and condenses the generated and evaporated gas, and 60 is a container for recovering the condensed components. Moreover, 61 is a sealing seal, and 62 is a fixture that secures the lid 54a to the container body 54.

[0091] On the other hand, as the recovered battery 55, for example, a rectangular lithium secondary battery that has undergone 300 charge-discharge cycles is prepared and the recovered battery 55 is housed in the aforementioned container body 54. After that, the lid 54a is positioned via the sealing seal 61, fixed and sealed using the fixture 62, and then the temperature controller 58 controls the heater 56 while raising the temperature inside the container body 54 to 350°C, maintaining that temperature for 30 minutes. Through this heating treatment, the safety valve opens under high pressure inside the aforementioned recovered battery 55, allowing the vaporized solvent within the recovered battery to disperse towards the condenser 59 side, where it is condensed and liquefied, and collected in the recovery container 60. This eliminates the risk of ignition during the battery dismantling operation. Additionally, it is effective to pre-score the recovered battery 55 prior to the heating treatment to facilitate dismantling.

[0092] Moreover, as shown in another embodiment in Fig. 19, a form is adopted where a vacuum pump 62 is attached to the recovery container 60 side, and when the interior of the container body 54 is reduced to about 100 mmHg, the efficiency of removing and recovering the solvent inside the battery can be increased.

[0093] In addition, when a portion of the recovered battery is opened by cutting, and the liquid inside the battery is vaporized for condensation and recovery, it can be performed as follows. As shown in Fig. 20 from a side view, in the case of a cylindrical secondary battery 55, an incision is made along the A-A line approximately 1 to 4 mm inward on the protruding surface side of the positive terminal 55a to partially open it, or the battery element can be extracted by cutting it open. When the solvent was recovered following the aforementioned Fig. 19 embodiment, similar results were obtained. Moreover, when the solvent was recovered using the embodiment illustrated in Fig. 20 (with the temperature inside the container body 54 being below 40°C), the recovery rate was 99%, and the risk of ignition during the battery dismantling operation was eliminated. Additionally, to reduce the possibility of ignition, it is effective to perform the cutting of the cylindrical secondary battery 55 while in a state cooled with liquid nitrogen or under an inert atmosphere.

[0094] Similarly to the aforementioned Embodiment 1, by carrying out the extraction and recovery of the solvent within the battery during the separation and recovery of the battery body as well as after the discharge processing and during the battery dismantling process, the working environment and safety for battery dismantling operations are significantly improved. Consequently, subsequent steps such as cleaning treatment of the separated battery dismantling products, heating treatment of the electrode elements, delamination processing of the active material layer, and treatment and recovery of the delaminated active material layer can proceed smoothly, leading to efficient waste processing with good productivity.

[0095] Embodiment 6

This embodiment relates to the separation and recovery of a laminated plate (such as a flexible wiring board) used in a battery package (battery pack) structure that incorporates multiple battery bodies. That is to say, it pertains to effective separation and recovery means for the constituent materials of wiring boards (such as copper foil, valuable metals including solder, inorganic substances like flame retardants, and resins), which are widely used in high-performance electronic devices and many other fields. In other words, this approach not only avoids issues such as environmental pollution but also achieves good separation efficiency, improving the recovery rate of precious metals while expanding the recycling and application of resins.

[0096] The laminated plate according to this embodiment is a composite formed by laminating materials subjected to different stress strains, yielding and causing internal destruction when a certain level of stress is exceeded. The laminated plate is characterized by a structure where a layer applying tensile stress is sandwiched between layers that do not apply tensile stress on both the upper and lower surfaces of this layer. During recycling, compressive force is applied in the opposite direction to the direction of the tensile stress acting on the laminated plate, nullifying the tensile stress and applying shear stress perpendicular to the surface of the expanded laminated plate, thereby breaking the layer that was under the aforementioned tensile stress.

[0097] For example, the laminated plate is composed of a metal layer and an insulating layer containing resin. Here, the metal layer is formed from uniformly processed copper plates with a thickness of 10  $\mu\text{m}$  to 1 mm by rolling, while the insulating layer uses glass fibers of thickness 10  $\mu\text{m}$  to 1 mm, filled with epoxy resin containing

triphenyl phosphate as a heat-resistant material after being subjected to tensile stress. Additionally, when viewed from above, the insulating layer containing glass fibers can take a structure where they are bundled into thin layers arranged in a grid-like manner and crossed alternately in the vertical direction.

[0098] The method for forming the aforementioned insulating layer and adhering it to the metal layer begins by bundling the glass fibers that serve as the framework of the insulating layer and fixing the edge portions of the lattice structure they create. The edge portions are then expanded in a direction of 0.1% to 10% to continue applying tensile stress. In this state, the epoxy resin containing approximately 0.1% to 20% of heat-resistant materials such as triphenyl phosphate is impregnated while sandwiching the glass fibers, and before drying, the metal layer (copper plate) is stacked and bonded onto it. After about 10 minutes to 10 hours, the applied tensile stress at the edge portions of this laminate is removed, and it is led to a press machine where the glass fibers protruding from the metal layer are cut off and removed using a cutting machine. Further, after drying for a period ranging from 1 hour to 5 weeks, it is cut and processed using a cutting machine.

[0099] During the cutting process, one piece is extracted, and the upper and lower metals are connected to a DC power supply to verify the insulation function. When a voltage of 100V is applied, the electric current flowing was less than 1 mA, below the detection limit of the measuring device. In the same manner, the insulation function of the laminate composed of multiple alternating insulating layers and metal layers was tested and evaluated after cutting, and it was found to be below the detection limit of the measuring device.

[0100] In addition, to apply a vertical impact to the laminated plate created by the same method, it was dropped from a height of 2 meters. Upon inspection, no changes were observed on the surface of the laminated plate, and there was no change in insulation function. Furthermore, after heating at 100°C for 2 hours, no changes were detected in appearance or insulation function.

[0101] Furthermore, similarly to the above description, after leaving the laminated plate at room temperature for more than one month under the same conditions, no changes were observed in insulation function, impact-related changes, or heat resistance when tested and evaluated. Therefore, assuming the recycling of the laminated plate with the aforementioned structure, compression force was applied in a direction that would shrink the glass fibers while fixing the edge portions. An external force was continuously applied from a perpendicular direction to the expanded surface of the laminated plate. As a result, it was confirmed that the copper plate began to bend sharply. After releasing the compression force from the edge portions and extracting the laminated plate, numerous cracks were observed in the glass fibers of the insulating layer, and separation of the metal layer was recognized.

[0102] In the case of the laminated plate with the above configuration, which forms a composite that yields and causes internal destruction at a certain level of stress, during recycling, a compressive force is applied in the opposite direction to the tensile stress acting on the laminated plate, thus nullifying the tensile stress. Shear stress perpendicular to the surface of the expanded laminated plate is then applied, allowing for the destruction of the layer

subjected to tensile stress. This makes it possible to separate and recover both metal components and non-metal components as useful resources. In summary, the laminated plate allows for material separation and recovery due to layering materials subjected to different stress strains, resulting in yielding and internal destruction above a certain stress level.

[0103] In the structure of the aforementioned laminated plate, one layer is subjected to tensile stress while laminating it with layers that do not experience tensile stress both above and below this layer.

[0104] A method for applying a compressive force in the direction opposite to the tensile stress acting on the laminated plate to cancel out the tensile stress, while applying shear stress to the surface of the laminated plate, thereby destroying the layer that previously experienced tensile stress.

[0105] A laminated plate utilizing resin in the layer subjected to tensile stress.

[0106] A laminated plate containing fibrous materials such as glass fibers and synthetic fibers in the layer subjected to tensile stress. This laminated plate includes a resin that becomes conductive upon applying pressure to the layer experiencing tensile stress.

[0107] Changing the tensile stress and compressive force through variations in the heating temperature of the laminated plate.

[0108] In the case of a laminated plate containing fibrous materials, recovery of the fibrous substances can be achieved by adding excess oxygen.

[0109] In the laminated plate according to this embodiment, although resin layers are cited as typical examples of the layers subjected to tensile stress, they can also be composed of fibrous materials, ceramics, mixtures of these, or resins that fill the gaps of these mixtures. The fibrous materials can broadly be categorized into natural fibers, chemical fibers, high-strength fibers, and highly elastic fibers. Natural fibers include cotton and hemp as plant fibers, as well as silk and wool as animal fibers. Chemical fibers can be divided into regenerated fibers like rayon and polynosic cupra, semi-synthetic fibers like acetate and triacetate, and synthetic fibers like nylon, acrylic, vinylon, polyvinyl chloride, polyvinylidene chloride, polyester, polyethylene, and polypropylene. High-strength fibers include asbestos, carbon fibers, glass fibers, aramid fibers, and ultra-high molecular weight polyethylene fibers, while polyurethane fiber is an example of a highly elastic fiber.

[0110] On the other hand, layers that do not experience tensile stress during processing can consist of metals such as copper and iron or resins that have conductivity.

[0111] Configuration Example 1

Fig. 21 shows a cross-sectional view of the Configuration Example 1 of the laminated plate, where 63 is a copper foil processed to a thickness of 100  $\mu\text{m}$  with a purity of 99.99%, and 64 with thickness 50  $\mu\text{m}$  is an insulating layer that fills around glass fibers 64a, which are subjected to tensile stress, with an epoxy resin 64b containing tricresyl phosphate as a phosphate ester. Here, the insulating layer 64, which includes the glass fibers 64a, is bundled in thin layers vertically, crossing each other in a lattice pattern of 1 cm squares, as shown in Fig. 22.

[0112] The formation of the insulating layer 64 and the adhesion or integration with the metal layer 63 begins by bundling the glass fibers of the insulating layer 64 into a grid pattern and fixing the edge portions of this bundle. The edge portions are then expanded by 1% while continuing to apply tensile stress. In this state, an epoxy resin containing 10% tricresyl phosphate is impregnated between the glass fibers, and before it dries, the metal layer 62 (copper foil) is laminated and adhered to both sides of the insulating layer 64. After approximately 2 hours, the applied tensile stress from the edge portions of this laminated structure is removed, and pressure is applied using a press machine to ensure adhesion. Glass fibers protruding from the metal layer 63 are then cut and removed with a cutting machine, followed by drying for an additional week before cutting to A4-sized pieces using a cutting machine.

[0113] One cut piece is taken out, and both metal layers 63 are connected to a direct current power supply, applying a voltage of 100V to test and evaluate the insulation function based on the electric current flowing through. It was found that the measured current was below the detection limit of the measuring device, at less than 1 mA.

[0114] In the same manner, a laminated body consisting of four metal layers 63 alternately adhered through the insulating layer 64 (with three insulating layers) was cut, and when the insulation function was checked, it was also found to be below the detection limit of the measuring device.

[0115] In addition, when the aforementioned metal layer in the 4-layer laminated plate was dropped from a height of 2 meters, delivering a vertical impact, there were no observable changes to the surface of the laminated plate, nor any changes to its insulation function. Furthermore, after heating at 100°C for 2 hours, no changes were detected in appearance or insulation function.

[0116] Next, after leaving the aforementioned metal layer in the 4-layer laminated plate at room temperature for 3 months, tests and evaluations of insulation function, impact-related changes, and heat resistance showed no changes.

[0117] Therefore, assuming the recycling of the 4-layer laminated plate, a compressive force was applied in a direction that would shrink the glass fibers while fixing the edge portions. An external force continued to be applied from a perpendicular direction to the expansive surface of the laminated plate. As a result, it was confirmed that the copper plate began to bend sharply. After releasing the compression force from the edge portions and extracting the laminated plate, numerous cracks were observed in the glass fibers of the insulating layer, indicating separation from the metal layer.

[0118] In this way, the laminated plate forms a composite that yields and causes internal destruction above a certain stress level. During recycling, a compressive force is applied in the opposite direction to the tensile stress acting on the laminated plate, canceling out the tensile stress, and shear stress perpendicular to the expanding surface of the laminated plate can be applied to destroy the resin layer, making it possible to separate and recover both metal and non-metal components as useful resources.

[0119] Configuration Example 2

In this example, a copper plate processed to a uniform thickness of 200  $\mu\text{m}$  with a purity of 99.99% is used as the metal layer, while an insulating layer is created by filling around glass fibers with a

diameter of 40  $\mu\text{m}$  that are subjected to tensile stress, using a phenolic resin containing tricresyl phosphate as a phosphate ester. The laminated plate is constructed in the same manner as in the Configuration Example 1. The formation of the insulating layer and its adhesion/integration with the metal layer begins by bundling the glass fibers of the insulating layer into a grid pattern and fixing the edge portions of this bundle. The edge portions are then expanded by 1% while continuing to apply tensile stress. In this state, a phenolic resin (resol type) dissolved in propyl alcohol containing 10% tricresyl phosphate is impregnated between the glass fibers, and before it dries, the metal layer is laminated and adhered to both sides of the insulating layer. After approximately 2 hours, the applied tensile stress from the edge portions of this laminated structure is removed, and pressure is applied using a press machine to ensure adhesion. Glass fibers protruding from the metal layer are then cut and removed with a cutting machine, followed by drying for an additional week before cutting to A4-sized pieces.

[0120] One cut piece is taken out, and both metal layers are connected to a direct current power supply, applying a voltage of 100V to test and evaluate the insulation function based on the electric current flowing through. It was found that the measured current was below the detection limit of the measuring device, at less than 1 mA.

[0121] In addition, in the same manner as in the Configuration Example 1, a laminated body consisting of four metal layers alternately adhered through the insulating layer (with three insulating layers) was cut, and when the insulation function was checked, it was also found to be below the detection limit of the measuring device.

[0122] Furthermore, regarding this 4-layer metal layer laminated plate, tests and evaluations such as drop impact testing and changes in appearance and insulation function after heating at 100°C for 2 hours showed results similar to those of the Configuration Example 1.

[0123] Next, after leaving the aforementioned metal layer in the 4-layer laminated plate at room temperature for 3 months, tests and evaluations of insulation function, impact-related changes, and heat resistance showed no changes.

[0124] Therefore, assuming the recycling of the 4-layer laminated plate, a compressive force was applied in a direction that would shrink the glass fibers while fixing the edge portions. The laminated plate was then dropped from a height of 2 meters while maintaining the surface with expansion horizontal. As a result, it was confirmed that the copper plate began to bend sharply. After releasing the compression force from the edge portions and extracting the laminated plate, numerous cracks were observed in the glass fibers of the insulating layer, indicating separation from the metal layer.

[0125] In this way, the laminated plate forms a composite that yields and causes internal destruction above a certain stress level. During recycling, a compressive force is applied in the opposite direction to the tensile stress acting on the laminated plate, canceling out the tensile stress, and shear stress perpendicular to the expanding surface of the laminated plate can be applied to destroy the resin layer, making it possible to separate and recover both metal and non-metal components as useful resources.

[0126] Configuration Example 3

In the case of the aforementioned Configuration Example 1, instead of using an epoxy resin containing tricresyl phosphate, a polyvinyl chloride containing 3% aluminum hydroxide was used. Under similar

conditions, laminated plates with 2 layers of metal and 4 layers of metal were created respectively. For the formation of the aforementioned insulating layer, glass fibers were bundled and crossed in a lattice pattern, fixing the edge portions of this substrate. The edge portions were expanded by 1% in a pulling direction while applying tensile stress, and while doing so, polyvinyl chloride containing 3% aluminum hydroxide was impregnated between the glass fibers by heating to below 150°C.

[0127] One cut piece from the laminated plate with 2 layers of metal was taken out, and both metal layers were connected to a direct current power supply, applying a voltage of 100V to test and evaluate the insulation function based on the electric current flowing through. It was found that the measured electric current was below the detection limit of the measuring device, at less than 1 mA. In addition, for the laminated plate with 4 layers of metal, it was confirmed that the insulation function was also below the detection limit of the measuring device.

[0128] Furthermore, regarding this laminated plate with 4 layers of metal, tests and evaluations such as drop impact testing, changes in appearance and insulation function after heating at 80°C for 2 hours, and insulation function after leaving at room temperature for 3 months showed no changes. Moreover, assuming the recycling of this 4-layer laminated plate, compressive force was applied in a direction to shrink the glass fibers while fixing the edge portions. The laminated plate was then dropped from a height of 2 meters while maintaining the surface with expansion horizontal. It was confirmed that the copper plate began to bend sharply, and after releasing the compressive force from the edge portions and extracting the laminated plate, numerous cracks were observed in the glass fibers of the insulating layer, indicating separation from the metal layer.

[0129] In this way, the laminated plate forms a composite that yields and causes internal destruction above a certain stress level. During recycling, compressive force is applied in the opposite direction to the tensile stress acting on the laminated plate to cancel out the tensile stress, and shear stress perpendicular to the expanding surface of the laminated plate can be applied to destroy the resin layer. This makes it possible to separate and recover both metal and non-metal components as useful resources.

[0130] Configuration Example 4

In the case of the aforementioned Configuration Example 1, cellulose fibers with a thickness of 10  $\mu\text{m}$  were bundled in groups of seven and twisted to form a fibrous substrate. An insulating layer was created using an epoxy resin containing 3% aluminum hydroxide that was impregnated into this substrate. Under similar conditions, laminated plates with 2 layers of metal and 4 layers of metal were created respectively.

[0131] One cut piece from the laminated plate with 2 layers of metal was taken out, and both metal layers were connected to a direct current power supply, applying a voltage of 100V to test and evaluate the insulation function based on the electric current flowing through. It was found that the measured electric current was below the detection limit of the measuring device, at less than 1 mA. Additionally, for the laminated plate with 4 layers of metal, it was confirmed that the insulation function was also below the detection limit of the measuring device.

[0132] Furthermore, regarding this laminated plate with 4 layers of metal, tests and evaluations such as drop impact testing, changes in

appearance and insulation function after heating at 100°C for 2 hours, and insulation function after leaving at room temperature for 3 months showed no changes.

[0133] In addition, assuming the recycling of this 4-layer laminated plate, compressive force was applied in a direction to shrink the glass fibers while fixing the edge portions. The laminated plate was then dropped from a height of 2 meters while maintaining the surface with expansion horizontal. It was confirmed that the copper plate began to bend sharply, and after releasing the compressive force from the edge portions and extracting the laminated plate, numerous cuts were observed in the cellulose fibers of the insulating layer, indicating separation from the metal layer.

[0134] In this way, the laminated plate forms a composite that yields and causes internal destruction above a certain stress level. During recycling, compressive force is applied in the opposite direction to the tensile stress acting on the laminated plate to cancel out the tensile stress, and shear stress perpendicular to the expanding surface of the laminated plate can be applied to destroy the resin layer. This makes it possible to separate and recover both metal and non-metal components as useful resources.

[0135] Configuration Example 5

In the case of the aforementioned Configuration Example 1, a mixed fibrous substrate was created by bundling together seven 50% cellulose fibers with a thickness of 10  $\mu\text{m}$  (seven fibers per bundle) and 50% glass fibers with a thickness of 30  $\mu\text{m}$  in a lattice structure of 1.5 cm square. An insulating layer was used that included an epoxy resin impregnated with 3% aluminum hydroxide. Under similar conditions, laminated plates with 2 layers of metal and 4 layers of metal were created respectively.

[0136] One piece of the laminated plate with 2 layers of metal, cut to A5 size, was taken out, and both metal layers were connected to a direct current power supply. A voltage of 100V was applied to test and evaluate the insulation function based on the electric current flowing through. It was found that the measured electric current was below the detection limit of the measuring device, at less than 1 mA. In addition, for the laminated plate with 4 layers of metal, it was confirmed that the insulation function was also below the detection limit of the measuring device.

[0137] Furthermore, regarding this laminated plate with 4 layers of metal, tests and evaluations such as drop impact testing, changes in appearance and insulation function after heating at 100°C for 2 hours, and insulation function after leaving at room temperature for 3 months showed no changes.

[0138] In addition, assuming the recycling of the aforementioned laminated plate with 4 layers of metal, the laminated plate was immersed in liquid nitrogen for 10 minutes, after which it was struck with a hammer leading to the separation of the insulating layer from the metal layer. This was due to rapid cooling, where the contraction of the metal layer could not follow the contraction of the insulating layer. Compressive forces acted in the direction where the fibers within the laminated plate were extended, canceling out tensile stress, and perpendicular forces acted on the expanding surface of the laminated plate, causing internal destruction of the insulating layer.

[0139] Furthermore, 1 gram of the separated insulating layer was cut

off and placed in a container with an ignition plug on the lid (made of SUS 316 with an inner diameter of 5 cm, depth of 10 cm, and thickness of 1 cm). After injecting oxygen at 20 atmospheric pressure and sealing it, the plug was ignited. After 10 minutes from ignition, when the lid was opened, 0.6 grams of solid materials consisting of glass fibers and powdered aluminum oxide remained.

[0140] In this way, the laminated plate forms a composite that yields and causes internal destruction above a certain stress level. During recycling, compressive force is applied in the opposite direction to the tensile stress acting on the laminated plate to cancel out the tensile stress, and shear stress perpendicular to the expanding surface of the laminated plate can be applied to destroy the resin layer. This enables the separation and recovery of both metal and non-metal components as useful resources.

[0141] Configuration Example 6

In the case of the aforementioned Configuration Example 1, a resin film mainly composed of polyvinylidene fluoride with a thickness of 100  $\mu\text{m}$  that exhibits conductivity when pressurized was used instead of the metal layer. Additionally, glass fibers with a thickness of 20  $\mu\text{m}$  were used as the substrate (0.5 cm square lattice), and an insulating layer impregnated with epoxy resin was utilized. Under similar conditions, laminated plates with 2 layers of metal and 4 layers of metal were respectively created.

[0142] One piece of the laminated plate with 2 layers of metal, cut to A5 size, was taken out, and both metal layers were connected to a direct current power supply. A voltage of 100V was applied to test and evaluate the insulation function based on the electric current flowing through. It was found that the measured electric current was below the detection limit of the measuring device, at less than 1 mA. For the laminated plate with 4 layers of metal, it was also confirmed that the insulation function was below the detection limit of the measuring device.

[0143] Furthermore, tests and evaluations conducted similarly to those in the Configuration Example 1 confirmed the same actions and effects.

[0144] Configuration Example 7

In the case of the aforementioned Configuration Example 1, glass fibers with a thickness of 20  $\mu\text{m}$  were used as the substrate (1 cm square lattice), and an insulating layer impregnated with silicone resin was utilized. Under similar conditions, laminated plates with 2 layers of metal and 4 layers of metal were respectively created.

[0145] One piece of the laminated plate with 2 layers of metal, cut to A5 size, was taken out, and both metal layers were connected to a direct current power supply. A voltage of 100V was applied to test and evaluate the insulation function based on the electric current flowing through. It was found that the measured electric current was below the detection limit of the measuring device, at less than 1 mA. For the laminated plate with 4 layers of metal, it was also confirmed that the insulation function was below the detection limit of the measuring device.

[0146] Additionally, tests and evaluations conducted similarly to those in Configuration Example 1 confirmed the same actions and effects.

[0147] This invention is not limited to the aforementioned illustrated embodiments and can take various modifications within the scope that does not deviate from the gist of the invention. For example, the

recycling method can similarly be applied to discarded batteries other than lithium-ion secondary batteries, such as nickel-metal hydride secondary batteries.

[0148]

[Effects of the Invention] As can be understood from the aforementioned explanation, according to the method for processing waste related to this invention, the generation of harmful substances containing fluorine or phosphorus components can be avoided while efficiently recovering valuable metal resources. That is, during the disposal of waste such as secondary batteries, it is possible to reduce or avoid environmental pollution and environmental load, providing a practical processing method with many advantages for effective resource utilization.

#### [Brief Description of Drawings]

[Fig. 1] It is a flowchart illustrating an example of the procedure for implementing this invention.

[Fig. 2] It is an explanatory diagram to describe an embodiment of the dismantling and separation of a battery package.

[Fig. 3] It is an explanatory diagram to describe an embodiment of the discharge processing of recovered batteries.

[Fig. 4] It is an explanatory diagram to describe an embodiment of the dismantling and separation of recovered batteries.

[Fig. 5] It is an explanatory diagram to describe an embodiment of the heating treatment of battery components separated from recovered batteries.

[Fig. 6] It is an explanatory diagram to describe an embodiment of the separation processing of battery components.

[Fig. 7] It is a flowchart illustrating an embodiment of metal recovery from battery components.

[Fig. 8] It is an explanatory diagram to describe an embodiment of the vibrational separation of battery components.

[Fig. 9] It is an explanatory diagram to describe an embodiment of the thermal vibrational separation of battery components.

[Fig. 10] It is an explanatory diagram to describe another embodiment of the discharge processing of recovered batteries.

[Fig. 11] It is a graph showing the electric current versus time during

the discharge processing of battery components.

[Fig. 12] It is an explanatory diagram to describe another embodiment of the discharge processing of recovered batteries.

[Fig. 13] It is a graph showing other examples of electric current versus time during the discharge processing of battery components.

[Fig. 14] It is an explanatory diagram to describe yet another embodiment of the discharge processing of recovered batteries.

[Fig. 15] It is a graph showing further examples of current versus time during the discharge processing of battery components.

[Fig. 16] It is an explanatory diagram to describe another embodiment of the discharge processing of recovered batteries.

[Fig. 17] It is an explanatory diagram to describe yet another embodiment of the discharge processing of recovered batteries.

[Fig. 18] It is an explanatory diagram to describe an embodiment of the volatilization and recovery processing of solvents in recovered batteries.

[Fig. 19] It is an explanatory diagram to describe another embodiment of the volatilization and recovery processing of solvents in recovered batteries.

[Fig. 20] It is an explanatory diagram to describe another embodiment of the dismantling and separation of recovered batteries.

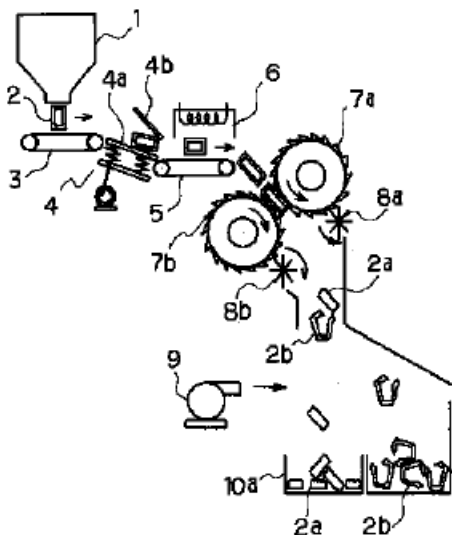
[Fig. 21] It is a cross-sectional view enlarging an example of the configuration of a laminated plate.

[Fig. 22] It is a plan view enlarging an example of the insulating layer configuration of a laminated plate.

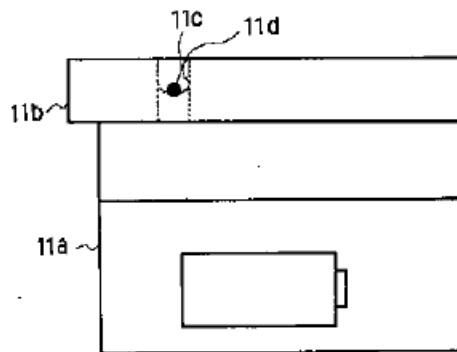
#### [Explanation of Reference Numerals]

- 1 ... supply hopper
- 2 ... battery package
- 3 ... first conveyor
- 4 ... battery rectifying means
- 5 ... second conveyor
- 6 ... heating device
- 7a, 7b ... rotary rolls
- 9 ... air classification blower
- 10a, 10b ... separation product containment containers

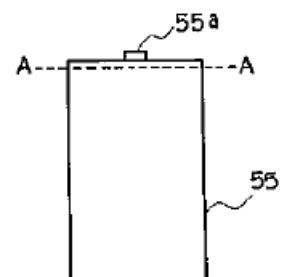
[Fig. 2]



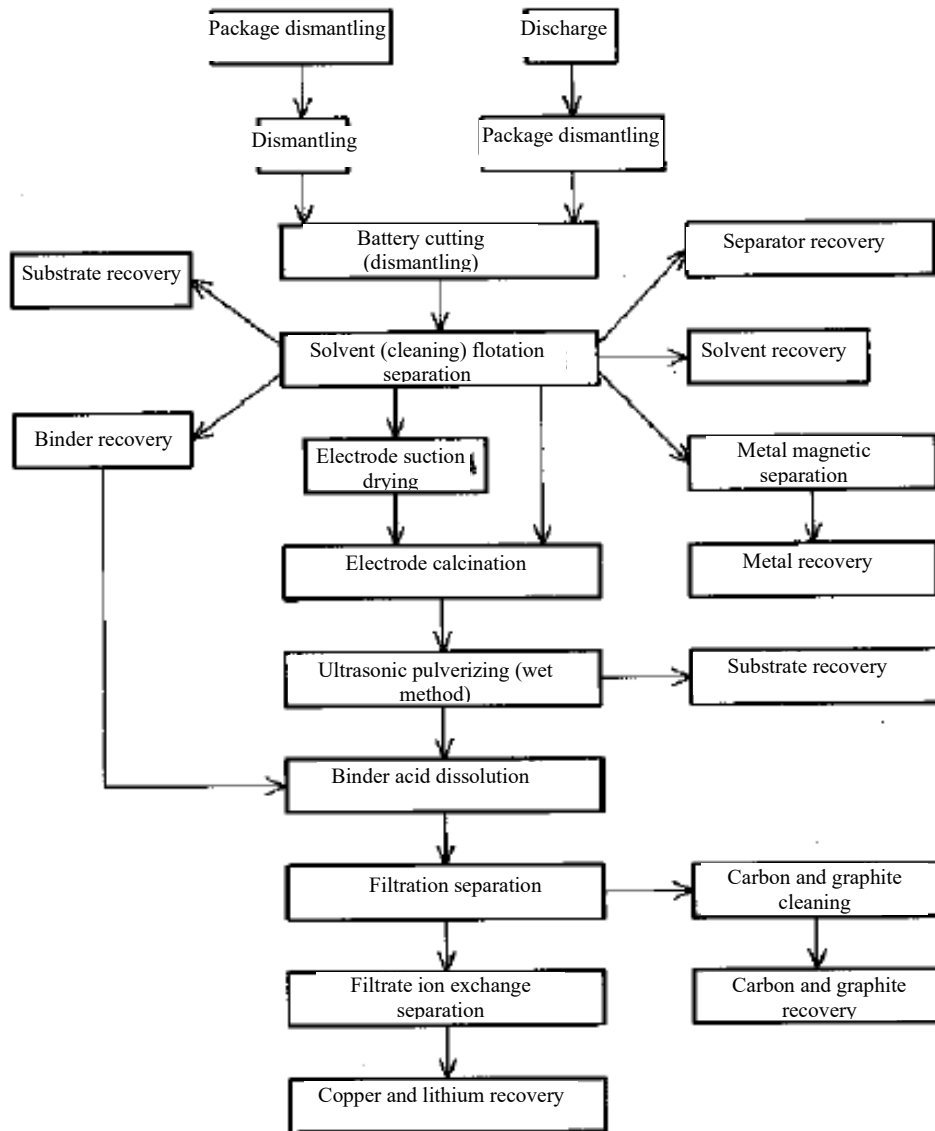
[Fig. 3]



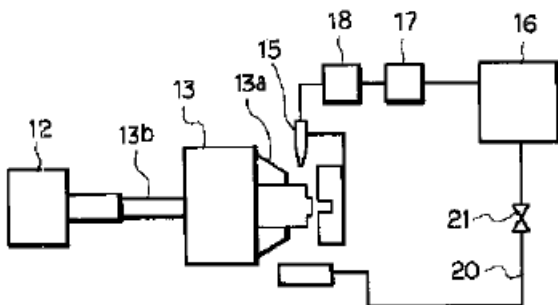
[Fig. 20]



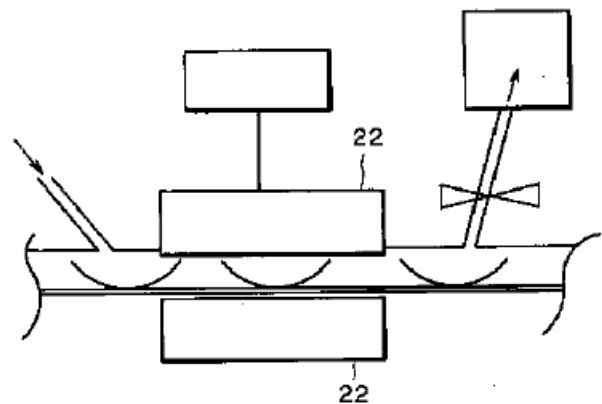
[Fig. 1]



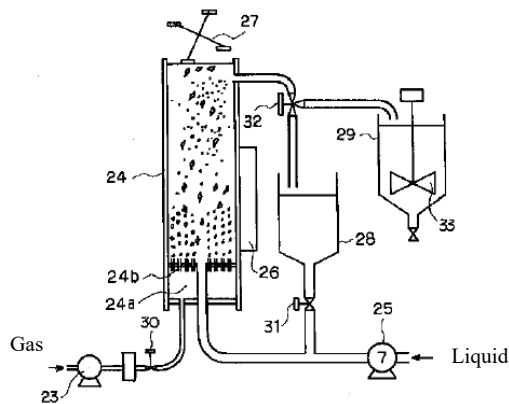
[Fig. 4]



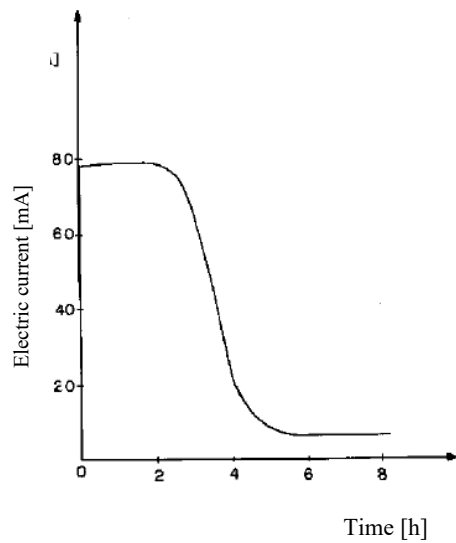
[Fig. 5]



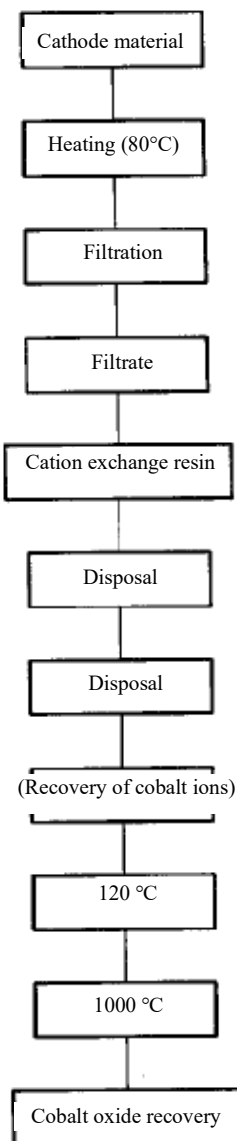
[Fig. 6]



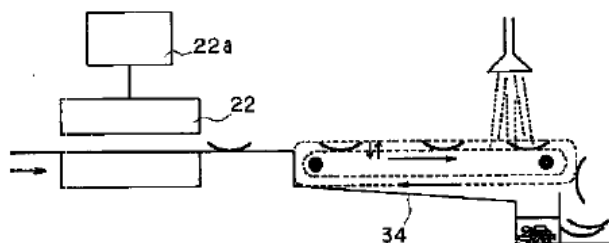
[Fig. 11]



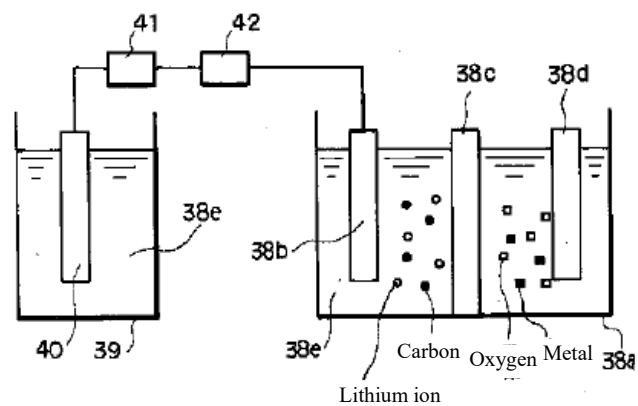
[Fig. 7]



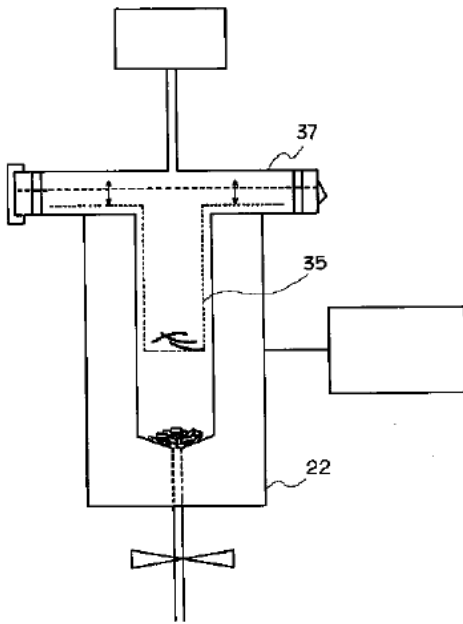
[Fig. 8]



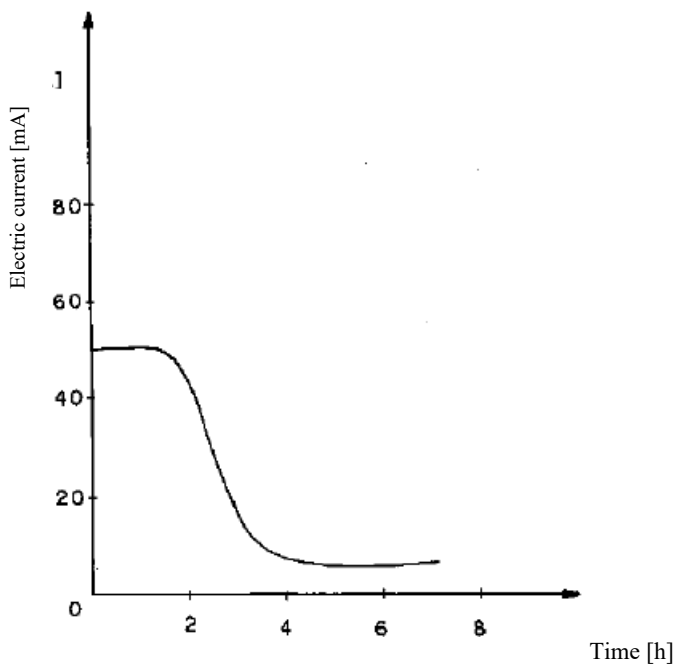
[Fig. 10]



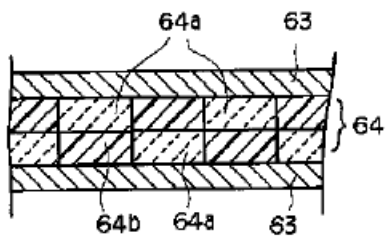
[Fig. 9]



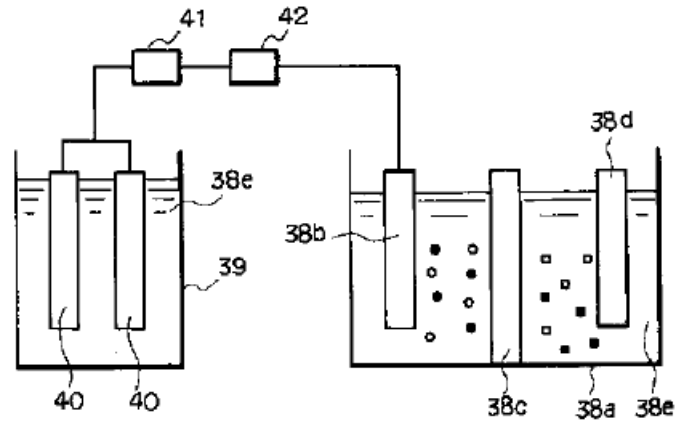
[Fig. 13]



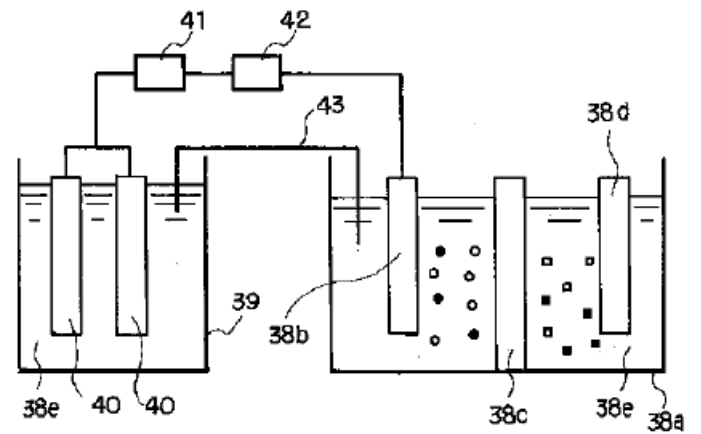
[Fig. 21]



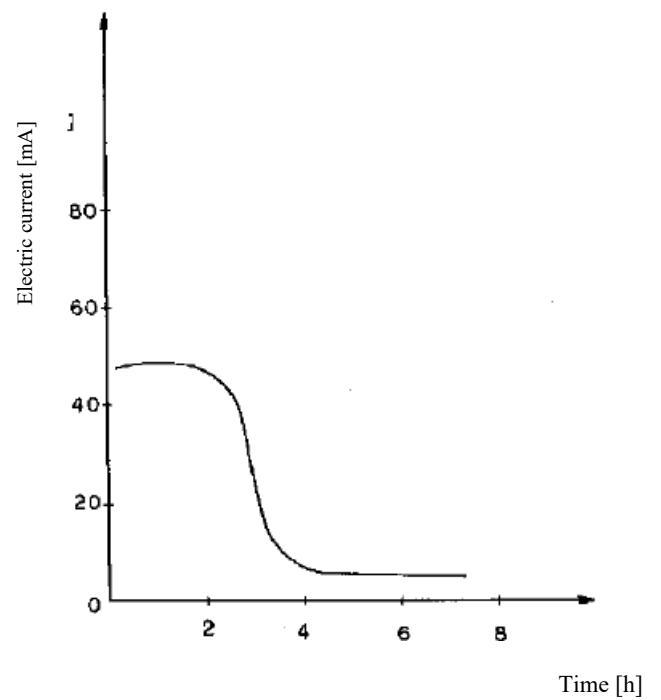
[Fig. 12]



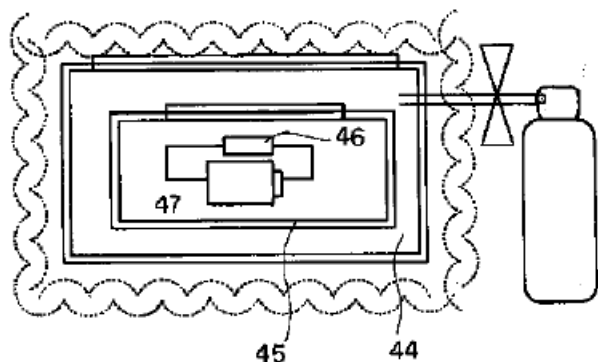
[Fig. 14]



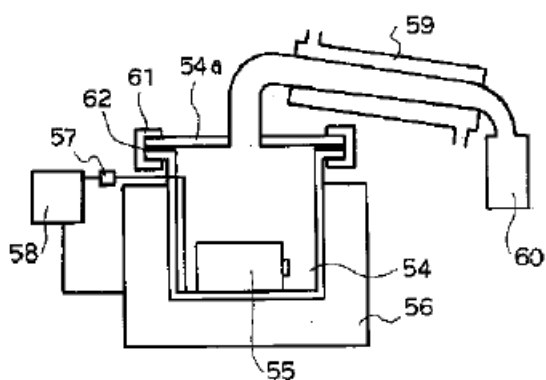
[Fig. 15]



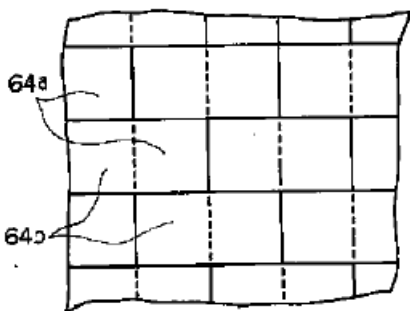
[Fig. 16]



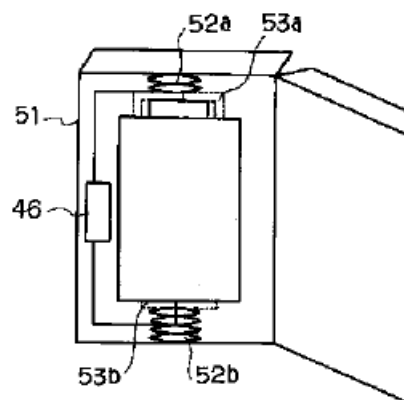
[Fig. 18]



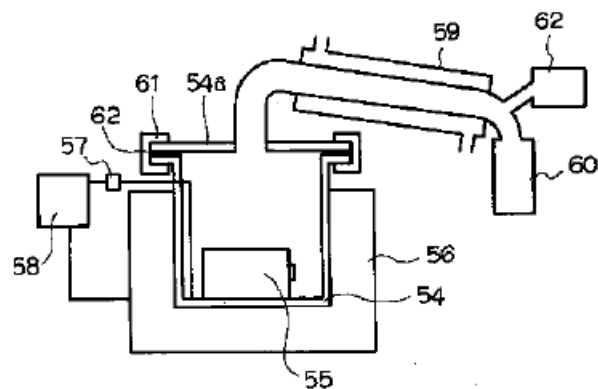
[Fig. 22]



[Fig. 17]



[Fig. 19]



Continuation of the front page

(72) Inventor: Naohiko Oyasato  
8 Shinsugita-cho, Isogo Ward, Yokohama City,  
Kanagawa Prefecture, Japan,  
Inside Toshiba Yokohama Office

(72) Inventor: Takeshi Gotanda  
8 Shinsugita-cho, Isogo Ward, Yokohama City,  
Kanagawa Prefecture, Japan,  
Inside Toshiba Yokohama Office

(72) Inventor: Hideo Kitamura  
8 Shinsugita-cho, Isogo Ward, Yokohama City,  
Kanagawa Prefecture, Japan,  
Inside Toshiba Yokohama Office

(72) Inventor: Izuru Komatsu  
8 Shinsugita-cho, Isogo Ward, Yokohama City,  
Kanagawa Prefecture, Japan,  
Inside Toshiba Yokohama Office

(72) Inventor: Masaru Hayashi  
1 Komukai Toshiba-cho, Saiwai Ward, Kawasaki City,  
Kanagawa Prefecture, Japan  
Inside Toshiba Research Consulting Corporation

(72) Inventor: Motoo Yabuki  
1 Komukai Toshiba-cho, Saiwai Ward, Kawasaki City,  
Kanagawa Prefecture, Japan  
Inside Toshiba Research Consulting Corporation

(72) Inventor: Masataka Konuma  
1 Komukai Toshiba-cho, Saiwai Ward, Kawasaki City,  
Kanagawa Prefecture, Japan  
Inside Toshiba Research Consulting Corporation

(72) Inventor: Kazunari Harada  
8 Shinsugita-cho, Isogo Ward, Yokohama City,  
Kanagawa Prefecture, Japan,  
Inside Toshiba Yokohama Office

(72) Inventor: Satoshi Kanazawa  
8 Shinsugita-cho, Isogo Ward, Yokohama City,  
Kanagawa Prefecture, Japan,  
Inside Toshiba Yokohama Office  
(72) Inventor: Kunihiro Sasaki  
8 Shinsugita-cho, Isogo Ward, Yokohama City,  
Kanagawa Prefecture, Japan,  
Inside Toshiba Yokohama Office

(72) Inventor: Yuko Baba  
8 Shinsugita-cho, Isogo Ward, Yokohama City,  
Kanagawa Prefecture, Japan,  
Inside Toshiba Yokohama Office  
(72) Inventor: Masaaki Morita  
1 Komukai Toshiba-cho, Saiwai Ward, Kawasaki City,  
Kanagawa Prefecture, Japan  
Inside Toshiba Research Consulting Corporation