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Recycling of Spent Dry Batteries for Deflection Yoke Core Applications

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Nomura Kohsan Corp. is producing oxides, such as $ZnMn_2O_4$, $ZnFe_2O_4$, and ZnO, by burning the used dry manganese cells and by sorting out the remnant materials. It is possible to use the recycled materials of the spent dry batteries as the raw materials of deflection yoke cores. Making high roasting temperature in the recycling system has an effect in reduction of the impurities. As a result, the loss of the cores using the recycled materials is lower. When using the recycled materials, it is required to add Mg $(OH)_2$, ZnO, and Fe_2O_3 in order to rectify the composition of the MnMgZn ferrite for deflection yoke core applications. Furthermore, in order to disappear $ZnMn_2O_4$ in the formation, it is necessary to control at higher calcining temperatures. The MnMgZn ferrite of using the recycled materials becomes loss equivalent to the conventional material. TDK Corp. is manufacturing the deflection yoke cores from 1996 using the material recycled from the spent dry batteries.
Keywords: used dry manganese cells, deflection yoke cores, MnMgZn ferrites, impurities.

Introduction

In Japan, a new law has taken effect from April, 2001. The law concerns the collection, transport, and recycling for designated household appliance waste products. It is prescribed in this law that retailers or makers must collect the portion of electrical appliances scrapped by the consumer, and must commercialize them. The target home electronics are air conditioners, television sets, electric refrigerators, and washing machines. The provided recycling rate is 50-60wt%. Recycling of the glass and metals used in TV sets is possible. In common TV sets, glass and metals are used about 15% and 57%, respectively. However, the deflection yoke cores which are the composition parts of TV sets are not yet reused. In the near future, it is expected that the prescribed recycling rate will be higher than 80-90wt%, and it is presumed that the deflection yoke cores will also become a major recycling object. The development of recycling systems and techniques by the electric-appliances maker and the measure for recycling by the society are activating[1, 2].

Not only the spread of color televisions but the arrival of the image information society have contributed to the expansion of the display market. Now, the annual shipment number of displays in the world is over 100 million sets. Moreover, the technology of displays is diversified. Not only the cathode ray tube (CRT) but liquid crystal display (LCD), plasma display panel (PDP), field emission display (FED), and organic electroluminescence (organic EL) have entered into the market. The market scale of CRT is large. The CRT is mainly used on the display exceeding 21 inches for the television sets and the personal computers. The market scale of LCD approaches that of the CRT, and PDP market also expand. The market scale of CRT is superior to others, because of the higher cost performance and the quality of images.

The CRT displays scan an electronic beam from the electron gun, shine the fluorescence film of the front of the cathode-ray tube, and produce pictures. One of the indispensable components for CRT is deflection yoke cores. Generally, MnMgZn ferrites are used for the material of the deflection yoke cores. The starting materials of the MnMgZn ferrites are magnesium, manganese, zinc, and iron oxides. On the other hand, the manganese dry batteries mainly consists of zinc, manganese, and iron. Therefore, a part of recycling material of the used manganese dry batteries is possible for the starting materials of MnMgZn ferrites. Nomura Kohsan Corp. collects mercury from used dry batteries. This company focussed on the application of zinc remnant materials after the process collecting mercury from the used dry cells. TDK Corp. has made a contract for joint development on April, 1992, and it established basic technologies by December, 1995[3]. The deflection yoke cores which used the recycling material of used dry batteries were manufactured from October in 1996. In this paper, the recycling method of used dry batteries and the application of the recycled material are reported

Recycling of Used Manganese Dry Batteries

Total Product and Reproduction Situation of Batteries

The ratio of batteries produced in Japan in 2000 is shown in Fig. 1. The quantity per year of the battery production in 2000 is 7,280 million pieces, among those, the ratio of primary batteries occupies 70% and the sum total of alkali and alkali manganese dry cells has become 40%. About 16 million kg per year of dry cells, which were used or were rejected by the manufacturers, were carried into Nomura Kohsan Corp.. The quantity is equivalent to about 23% of primary batteries currently consumed at home. Furthermore, the manganese dry cells occupy 75wt% in the batteries gathered by Nomura Kohsan Corp.. The alkali manganese cells are the 2nd, and the weight ratio is 23wt%. Most dry cells gathered into Nomura Kohsan Corp. can be recycled to ferrite materials. The composition of a common manganese dry cell is shown in Fig. 2. The iron, zinc, and manganese are used about 70wt% in the manganese dry cell. When the used manganese dry cells were burned, iron, zinc, and manganese become oxides, and papers and moisture are lost. However, when using the oxides for the ferrite materials, it is assumed that the impurities, such as

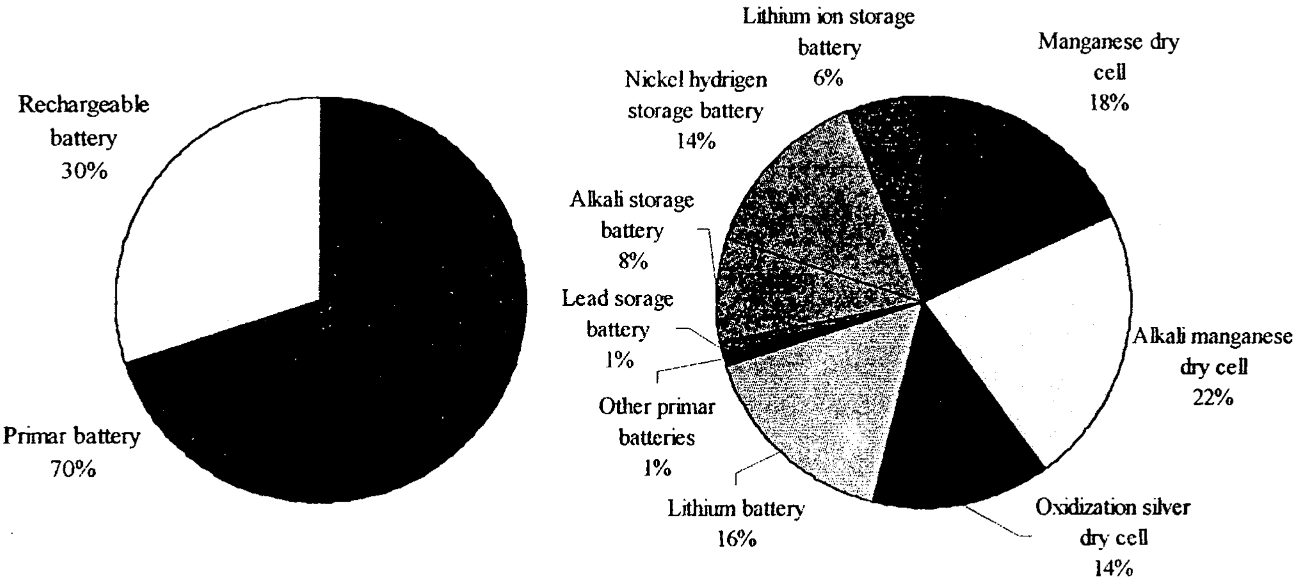

Fig. 1 Ratio of the battery produced in Japan in 2000.

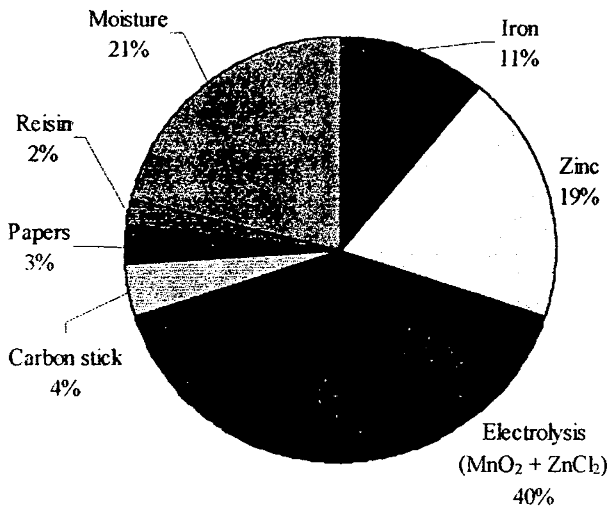

Fig. 2 Composition of a common manganese dry cell.

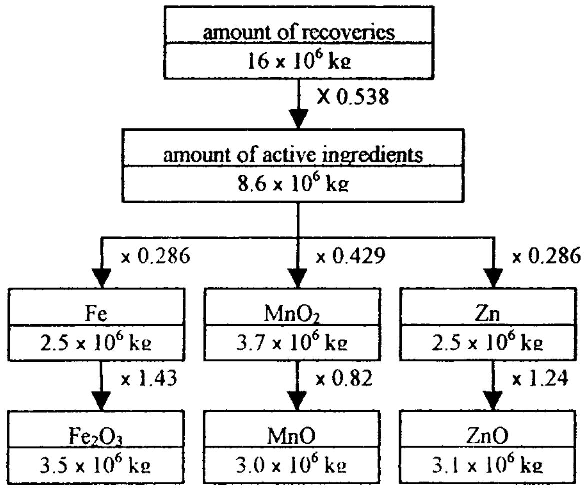

Fig. 3 Reproduction situation of the used dry cells in 2000.

remained carbon, are problems. The reproduction situation of the used dry cells in 2000 is shown in Fig. 3. If the amount of recoveries exceeds about 50% of that of production, the reproduced quantity will satisfy mostly the amount of MnO and ZnO in order to produce deflection yoke cores in Japan.

Recycling Technology of Manganese Dry Cells

Research on the recycling of manganese dry cells has been under way for some time[4]. It was reported that manganese or zinc were refined from the acid which melted the used dry cells. This technique was not put into utilization due to the cost problem. The adopted technique is simple compared to the process described previously, and is excellent in cost performance. The process is shown in Fig. 4. In this system, iron, zinc and manganese from the used-dry-cells are not turned into metals but serve as oxides. In order to fulfill the magnetic characteristic of the electronic components, the mixing prevention and reduction of impurities are important. The impurities of the raw materials are reduced through the procedure of magnetic separation, roasting and screening, and the produced recycling materials are suitable as the starting materials of deflection yoke cores. Especially, the 2nd roasting is important, because of reducing Cl and C. The composition of the materials produced using this system is shown in Table 1. Many various impurities are contained in the recycled materials. Therefore, it cannot use for the

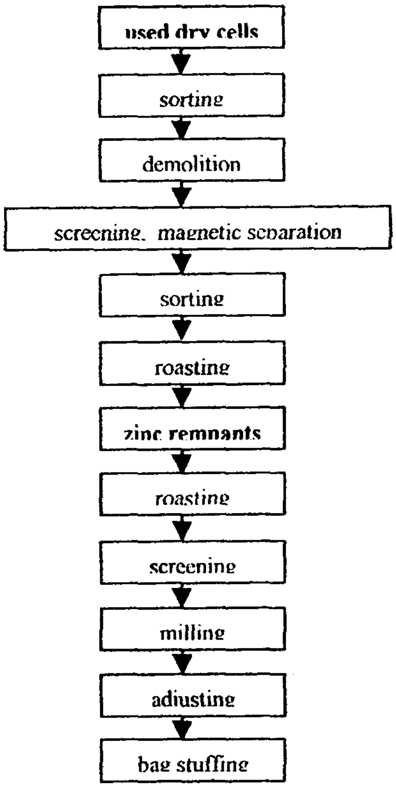

Fig. 4 Process of the recycling system.

power applications using MnZn ferrites which has the high characteristic.

Application for Soft Ferrite Materials

Experiment Method

The samples were prepared using the industrial materials and the recycled ones from the used dry cells. The industrial materials were Mg $(OH)_2$, ZnO, Mn_3O_4, and Fe_2O_3. On the other hand, the recycled materials were in the state of $ZnMn_2O_4$, $ZnFe_2O_4$, and ZnO. These were weighed to compose MnO=4.0wt%, MgO=11.5wt%, ZnO=14.0wt%, and Fe_2O_3=70.5wt%. In the case of using the recycled materials, Mg $(OH)_2$, ZnO, and Fe_2O_3 were added in order to rectify the composition. They were mixed, calcined at 1000°C for 1 hour, and milled for 10 minutes with dry vibration type. The ferrite powders were granulated using 0.6wt% PVA, and pressed into toroids at 98MPa. The green bodies were fired at 1320°C for 2 hours in air.

Formation during calcining

In the case of using the industrial materials, the formation is shown in Fig. 5. On the other hand, when the sample is created from the recycled materials, the formation is shown in Fig. 6. The products differ by the case of using industrial materials and that of using recycled materials at 900°C or less, because $ZnMn_2O_4$ contained in

Table 1 Composition of the materials produced with recycling system.

Element	Value
MnO	43.56wt%
ZnO	43.02wt%
Fe_2O_3	4.00wt%
SiO_2	4000 - 7000ppm
CaO	500 - 1000ppm
MgO	560 - 830ppm
Na_2O	900 - 1000ppm
K_2O	4300 - 7000ppm
C	800 - 1200ppm
Cl	700 - 3200ppm
SO_4	5100 - 8300ppm

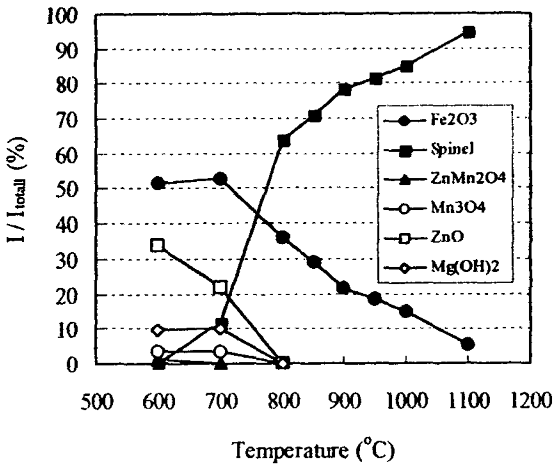

Fig. 5 Temperature dependence of the X ray intensity of the formation from the industrial materials.

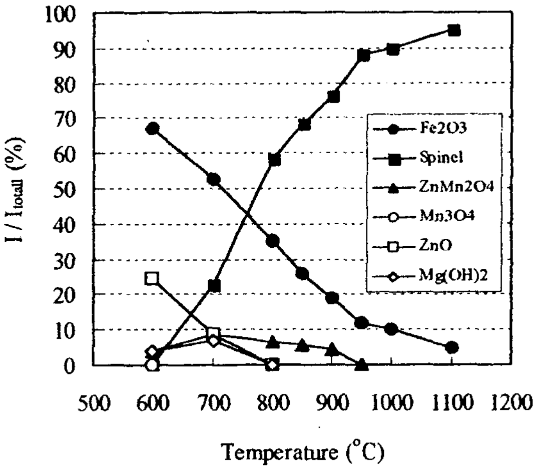

Fig. 6 Temperature dependence of the X ray intensity of the formation from the recycled materials.

Table 2 Impure amounts in the recycled materials and electromagnetic characteristics.

Roasting condition			
Number of times	2	2	1
2nd roasting temperature	high	low	
Impure amount			
Cl [wt%]	0.28	1.70	5.40
C [wt%]	0.09	1.74	7.73
Electromagnetic properties			
Initial permeability at 23°C	370	365	335
Saturation magnetization at 23°C [mT]	243	238	234
Coercive force at 23°C [A/m]	41.5	48.0	48.8
Core loss at 32kHz, 100mT, 100°C [kW/m^3]	215	228	272

the recycled materials does not disappear at higher temperatures. Furthermore, the formation does not differ by the case of using industrial materials and that of using recycling materials above 1000°C. When using the recycling materials for the ferrite cores, it is necessary to set up higher calcining temperatures.

Influence of Impurities

In the manganese dry cells, $ZnCl_2$ is used for electrolysis, papers and resin are used for the separators and the carbon stick is used for the collectors. It is assumed that Cl and C remains in the raw materials by the method of recycling, and have bad influence on microstructures[5] and magnetic characteristics of the ferrites. In this experiment, Cl or C amounts in the recycled materials was adjusted by changing roasting conditions. The impure amounts in the recycled materials and the electromagnetic characteristics of the sintered ferrite are shown in Table 2. When the amounts of Cl and C increases, the initial permeability and saturation magnetization are lower, and the core loss is higher. By some examination, it is important to set the content of Cl to 3200ppm or less and to control the content of C to 1200ppm or less. For that purpose, it is effective to repeat the roasting in the recycling process of the used manganese dry cells, and to control comparatively higher temperature during roasting. By doing so, the electromagnetic characteristic of the ferrite cores from the recycled materials is equivalent to that of the lowest grade among three conventional deflection yoke cores. However, the cost performance is high. The key to improving the electromagnetic characteristics of ferrites is to further reduce the amounts of some impurities in the recycled materials.

Conclusion

Burning the used manganese dry cells forms oxides, such as $ZnMn_2O_4$, $ZnFe_2O_4$, and ZnO. When the recycled materials of the used manganese dry cells are used for the starting materials of MnMgZn ferrites, the calcining temperature is higher than that of using industrial materials, in order to extinguish $ZnMn_2O_4$. The decrease of Cl and C contents in the recycled materials is effective in lowering the core loss of the ferrites. The recycled materials which fully roasted the used manganese dry cells can be used as the raw materials of deflection yoke cores.

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