Applicability of Oxalic Acid for the Removal of Paint from Used Beverage Aluminum Cans (UBC)*

Sungoh LEE**, Suntae KIM****

Nampyo KOOK*** and Myongjun KIM****

Aluminum cans can be reused into can body material through the melting process. However, the melting process has some problems, such as the accumulation of impurities and a decrease in the molten metal yield by titanium oxides from the paints on the surface of used beverage aluminum cans (UBC). Therefore, in order to reuse UBC as can material, paints, which are composed of resin and titanium oxides must be removed by pre-treating with a technical process. This study used organic oxalic acid for the swell-peeling process of paints on UBC. Oxalic acid reacted effectively with paints at 100°C and pH range of 1.5 and easily removed most paints from the surface of UBC. However, some UBC selectively reacted with oxalic acid and the paints were swelled from the surfaces of UBC slowly due to different polymer materials used to produce the paints.

1. INTRODUCTION

Recycling aluminum material could save about 95% energy compared to producing aluminum through smelting or refining bauxite. In order to produce 1 kg of aluminum, 56 KW of energy is used whereas only 2.5 KW of energy is needed to process the scrap aluminum collected. Thus, in countries such as Korea where all bauxite is imported, the recycling of waste aluminum scraps is important¹⁻²⁾.

In Korea, many studies are being conducted with keen interest on the recycling of UBC. UBC are separated, sorted and smelted to produce Al-ingots, which are supplied to aluminum manufacturers. However, resins and paint on cans cause low rate recovery of UBC and reduce the purity of the products, and therefore they are used for low grade base material such as die-casting³⁻⁶⁾.

Polymers and organic chlorides, the compounds that paints, react with highly oxidizing aluminum and show characteristic volatility, resulting in a low recovery rate. Also, oxidized compounds such as TiO₂ added as the

paint's pillar material, melt with aluminum, lowering the purity of aluminium^{1,2,6,7)}. Thus, in order to solve these problems, the process of eliminating paint using a rotary kiln at low temperature to delacquer paints was developed and is recently being used. Although the recovery rate can be increased through the process of delacquering, the problems with energy and impurities (TiO₂) can not be effectively eliminated. Thus, in order to solve these problems, studies on an organic chloride reagent to swell-peel paints are under progress but are still at the research stage⁸⁻⁹⁾.

Instead of using the delacquering process through heating, our experiment was conducted using a hydrothermal process for the swell-peeling of paint from the surface of UBC, but which does not dissolve paints. In addition, developing a solvent that is effective on swell-peeling and is environmentally friend can maximize the effectiveness of recycling UBC and UBC can be used to virgin material for the can manufacturing as can to can.

2. EXPERIMENTAL

2.1 Sample and chemical

The experiment was conducted with oxalic acid (H₂C₂O₄ · H₂O) as the solvent for the swell-peeling process and ammonia to control pH in distilled-deionized water. The sample used for used beverage aluminum cans (UBC) came from five most popular brand products of Coca Cola Co. (CC: Coca Cola, KC: Kin Cider, Cl: Coca Cola Light,

* This paper was presented at the 5th International Symposium on East Asian Recycling Technology in Tsukuba City, Japan, June 15-17, 1999

** Dept. of Environmental Eng., Chodang Univ.

*** Dept. of Environmental Eng., Hanlyo Univ., Korea

**** Dept. of Mineral and Energy Resources Eng., Chonnam Nat'l Univ., Korea

平成12年 3月15日受理

HT: Hwan Ta and PR: Powerade); the aluminum cans were cut into sample pieces of 1.5 cm × 1.5 cm and used for the experiment.

2.2 Experimental conditions

A 1L three-necked flask was used as the reactor with a stirrer in a temperature controllable water bath. The experimental conditions were as follows:

- Reaction temperature: 27~100°C
- Concentration of oxalic acid: 0.01~0.5 mol/L
- Initial pH range: 1.43~3.0
- Agitation speed: fixed at 250 rpm and not agitated

The efficiency of removal (%) was calculated by the equation; $=100 (W_i (\text{initial weight of sample}) - W_f (\text{final weight of sample}) / W_i$, and measured by the naked-eye.

3. RESULTS AND DISCUSSION

3.1 Surface Image analysis of UBC

Fig. 1 shows the image analysis on the surface of UBC with a X-ray diffractometer. Fig. 1 (a) shows the outside surface of UBC which is treated without a base coating but only treated with a varnish after printing of the label on the Al surface. Fig. 1 (b) shows the outside surface of an other sample which is treated with white base coating for the clear coloring of label. TiO_2 involved in white base coating materials was detected by XRD. Fig. 1 (c) shows the inside surface of UBC which is treated with only a lacquer. Therefore, there is no TiO_2 on the samples in Figs 1 (a) and 1 (c). This TiO_2 is the main impurity for the recycling of UBC as can-to-can.

3.2 Effect of temperature

Fig. 2 shows the reaction relationship between oxalic

Fig. 1 Image scanning (actual size) and XRD analysis of UBC

Fig. 2 The effect of temperature on the removal of paint from UBC (Oxalic acid concentration: 0.3 mol/L Initial pH: 1.54, Reaction time: 15 min)

acid and paints according to temperature. The experiment was conducted with 0.3 mol/L oxalic acid solution (initial pH 1.54) which was agitated at 250 rpm with temperatures ranging from 27~100°C. The swell occurred slowly at temperatures below 85°C due to low activity of oxalic acid⁹⁻¹⁰. However, when temperature was raised to 100°C, except in a few specimens, the swell-peeling of paint occurred fast from the surface of UBC and, in particular 100% paints on Cl, HT samples and 95% on KC sample were eliminated. The removal efficiency of the paints differed depending on the paint used.

3.3 Effect of oxalic acid concentration

Fig. 3 shows the removal efficiency of paint as a function of the changes in the oxalic acid concentration. The concentration changed at the reaction temperature of 100°C and the reaction time of 15 min. When the concentration of oxalic acid was 0.1 mol/L (initial pH 1.78), the swell-peel reaction did not occur. However, when the concentration was increased to 0.2 mol/L (initial pH 1.69), a part of the can surface showed the process of swell-peel, and about 90% of Cl and PR was eliminated. When the acid concentration was further increased to 0.5 mol/L (initial pH 1.43), all the can surfaces showed swelling and peeling occurred within 15 min. Swelling began fast and peeling progressed the fastest in Cl and PR samples, not only according to the reaction temperature but also to the change in the acid concentration. These results are due to the characteristic of paints applied to the can surface; and

Fig. 3 The effect of oxalic acid concentration on the removal of paint from UBC (Temperature: 100°C, Reaction time: 15 min)

unlike other cans, CI and PR cans reacting easily with oxalic acid may be due to white resin not being used.

3.4 Effect of pH

Fig. 4 shows the removal efficiency of paint from UBC as a function of pH. The experiment was conducted at the reaction temperature of 100°C with a concentration of 0.3 mol/L of oxalic acid for the reaction time of 15 min. The changes in pH greatly affect oxalic acid when the acid dissociates in the solution. At the pH 1.0, $\text{H}_2\text{C}_2\text{O}_4$ molecule and HC_2O_4^- ion are present in equal amounts; at the pH ranging from 2.3 to 3.0, HC_2O_4^- is the prevalent ion showing about 90%; however, when pH is at 4.0, HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$ are present in equal amounts, and when the pH exceed 4.5, $\text{C}_2\text{O}_4^{2-}$ is the major ion reacting in the solution¹⁰⁻¹¹). In other words, when oxalic acid reacts with metal ions and forms the oxalate complex, the range of pH where the reaction occurs is around 2.5. However, in this experiment, when the pH was changed at the same concentration, the process of swelling and peeling decreased as the pH increased¹¹). It was considered that the increased reactivity at lower pH was affected mainly due to effective targeting by the hydrogen ions dissociated. Also, at pH lower than 2.5, the formation of $\text{Al}(\text{C}_2\text{O}_4)_n^{3-2n}$ ($n=1, 2, 3$) tends to occur slowly, suppressing the elution of Al ions from the can surface or severed surface. Also, TiO_2 , which is the pillar of white paint, dissolved slowly showing of 13.8 mg/l for 20 min. This means that oxalic acid effectively reacted with the free radical of the polymer better than

Fig. 4 Speciation of oxalate solutions and removal efficiency of paint from UBC as a function of pH (Temperature: 100°C, Reaction time: 15 min)

TiO_2 and Al metal in this system.

3.5 Observation of surface

Fig. 5 shows the change in the surface of UBC according to reaction times. Using a PR sample, the specimen, which reacted at 0.3 mol/L (pH 1.54) oxalic acid concentration at the reaction temperature of 100°C, was observed through an optical microscope. Fig. 5 (a) is a photo of the UBC surface before going through the

Fig. 5 Optical micrographs on the surface of UBC (Temperature: 100°C, Oxalic acid concentration: 0.3 mol/L) (a) raw UBC (b) after 3 min (c) after 8 min (d) after 15 min

Attacking of acid

Acids

Swelling & peeling

Fig. 6 Schematic of swell-peeling of paint on UBC

hydrothermal process, in which the surface shows very roughly applied paint and many small hilly bumps are seen. Fig. 5 (b) is a photo of the UBC surface reacted 3 min and shows oxalic acid corroding the surface as the black dots are formed on parts of the surface. Fig. 5 (c) is a photo of UBC reacted 8 min, and the swelling are seen on parts of the surface. Thus, it was considered that the process of swell occurs due to the cutting off of the crosslinked paint and resin molecules by the attacking oxalic acid, and the peeling was accelerated by hydrogen gas generated on the surface of Al reacted with oxalic acids. (Fig. 5) (d))

3.6 The Phenomena of swell-peeling

Fig. 6 shows the phenomena of swell-peeling by using oxalic acid. The swell-peeling reaction can be illustrated as followed reaction steps. Firstly, the polymer chains were cut by the activated hydrogen ions attack generated by dissociation of oxalic acid on the surface of paints (equation 1). The paint was swelled and peeled by generated hydrogen gas as seen in equation 2. The generated hydrogen gas accelerated the swell-peeling of paint due to swelling force > adhesion force.

CONCLUSION

The present study used oxalic acid in the form of organic acid for the swell-peeling process of paints on UBC. At 100°C, oxalic acid reacted better with paint with pH about 1.5 than with pH about 2.5. However, some UBC selectively reacted due to different manufacturing processes. CC covered with white resin was especially slow to swell whereas Cl and HT swelled rapidly, at the same experimental condition. The process of swelling occurs due to the cutting off of the crosslinked paint and resin molecules by oxalic acid attacking, and the peeling was accelerated by hydrogen gas generated on the surface of Al reacted with oxalic acid. From these results, oxalic acid can be considered as a swell-peeling reagent of paints and can increase the efficiency of aluminum can recycling.

REFERENCES

- 1) Shin, P. S., Resources Recycling, Chonnam Nat'l Univ. Press, 1993
- 2) Shin, P. S. and Lee, S. O., Keyword of Recycling, Chonnam Nat'l Univ. Press, 1997
- 3) Park, H. K., Kim, J. S., Kim, S. D., Lee, H. I. and Kim, C. J., Proceedings of the 2nd International Symposium on East Asian Resources Recycling Technology, 1993, Seoul, Ed. by J. H. Oh, p. 386-402
- 4) Oosumi, K., Trans. Mat. Res. Soc. Japan Vol. 18A, 1993, p. 197
- 5) Kim, J. S. et al., Report of KIGAM, Korea Resources Recovery and Reutilization Corporation, 1996
- 6) 浦 幹夫, 塗料工學, Vol. 78, No. 42, 1994
- 7) 大遇研治, 金屬, Vol. 66, No. 2, 1996
- 8) Patent of Japan, 平 03-290475
- 9) Fujisawa, K. Kogishi, T. Oosumi, K. and Nakamura, T., J. of MMI of Japan, Vol. 113, No. 12, 1997
- 10) Lee, S. O., Oh, J. K. and Shin, B. S., J. of MMI of Japan, Vol. 115, No. 11, 1999 (accepted)
- 11) Papias, D., Taxiarchou, M., Paspaliaris, I. and Kon-topoulos, A. (1996): Hydrometallurgy, Vol. 42, p. 257-265.