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A New Chemical for the Separation of the CRT Panel Glass from its Funnel

Ki-Won Lee[1], Ji-Young Byun[2], Kyong-Tae Kim[2], and Jong Kee Oh[2]

[1] JIWON TECH, 16BL-25, Banwull Industrial Complex, #451-1, Moknai-Dong, Ansan-City, Kyungki-Do, Korea
[2] Metal Processing Research Center, Korea Institute of Science and Technology, #39-1 Haweolgok-Dong, Sungbuk-Ku, Seoul 136-791, Korea

The first step for recycling the CRT bulb is to remove frit seals between the panel and funnel. For this purpose, various kinds of methods have been used. One of those is to use the nitric acid, which is a proven technology and widely used in CRT-making industries. The process, however, has a problem of NOx generation. Such a drawback can be overcome by using a new chemical. This new chemical can remove the frit without NOx generation. This paper describes the dissolution ability of the chemical for lead and zinc oxides and the application to the separation of the CRT panel from its funnel.
Keywords: CRT, Frit glass, Recycling

Introduction

The present paper describes a new chemical for dividing CRTs (cathode-ray tubes). The cathode-ray tube, used as an image receiver incorporated in television sets or computers, is a glass structure composed of a panel and a funnel.

CRTs are fabricated by sealing together the panel glass supporting the phosphorescent display screen of the tube and the funnel glass having an electrically conductive interior coating. In order to seal the components together, a high-lead solder glass called as the frit is used. The frit glass mainly consists of PbO, B_2O_3, and ZnO. The sealing glass is mixed with a binder like nitrocellulose and a solvent like amyl acetate to form a paste. This glass paste is applied to the edges of one part (either the panel or the funnel) in the form of a ribbon, which is then dried. The remaining part is placed in contact with the dried paste and the assembly is heated to evaporate the solvent, burn out the binder and fuse the sealing glass [1].

For recycling or reusing the CRT glass, the panel part should be separated from the funnel part and the frit also removed due to the difference of lead content between three kinds of glasses. The panel is made of a lead free or a 2% to 3% lead content glass with a trend toward increasing use of the no-lead composition. The funnel is made of a lead-containing glass for preventing leakage of X-rays in which the lead content is about 24%. The lead content in the frit is approximately 70-80%.

In case of the disposal of CRTs, television and computer CRTs present a problem due to their growing magnitude in the waste stream as well as their role as a major source of lead in municipal solid waste. Lead's toxic effects have been known, specially its effects upon the development of children. In 2000, CRTs are estimated to contribute about 30% of all lead in municipal solid waste (98.7% of lead in electronics wastes) [2]. When CRTs are disposed in landfills, increased concentration of lead in landfill leachate may occur. According to a recent study [2] which was conducted to evaluate lead leachability from CRTs using TLCP (Toxicity Characteristic Leaching Procedure), the most hazardous part was found to be the frit. Samples containing the frit seal were reported to have lead leaching levels nearly 50 times those without the frit. This indicates that the frit portion in CRTs should be removed before its disposal. When recycled CRT glass is returned to the CRT making industry as a raw material, the frit should be also removed, because the glass containing the frit would contaminate the raw material and the control of glass composition would be difficult. And the panel portion and the funnel portion need to be handled separately.

Several dividing methods of the panel glass from the funnel glass have been reported [2-6]. The methods can be categorized by physical and chemical methods. The well-known physical methods are (a) cutting the frit part by a diamond saw [6], (b) using a heating chamber [6], and (c) using heating wires and bands [3,4]. All physical methods have a common problem which is not possible to remove the frit portion adhered on the edges of the panel and funnel, though the separation of the panel from the funnel is possible. In addition, the cutting method has another disadvantages; generation of lead containing dust and difficulty to treat a lot of CRTs. Use of the heating chamber can apply to massive treatment of CRTs, but can not apply to treat small amounts of CRTs due to economical aspect. Use of heating wires or bands has also a limitation. It is difficult to separate the panel portion from the funnel portion exactly, so cracks may be generated inside the glass portions on the funnel and/or the panel.

A well-known chemical method is to use the nitric acid. This method has been applied to salvage CRTs in CRT-making industries. Nevertheless, the process has some problems; the generation of HNO_3 mist and NOx, the bad working conditions, the corrosion of environmental equipment, the necessity of a plant for treating the waste acid, etc. Due to such problems, this method is difficult to be adopted to recycle television and computer CRTs.

Thus, the present study is concerning on the chemical method to separate the panel glass from the funnel without

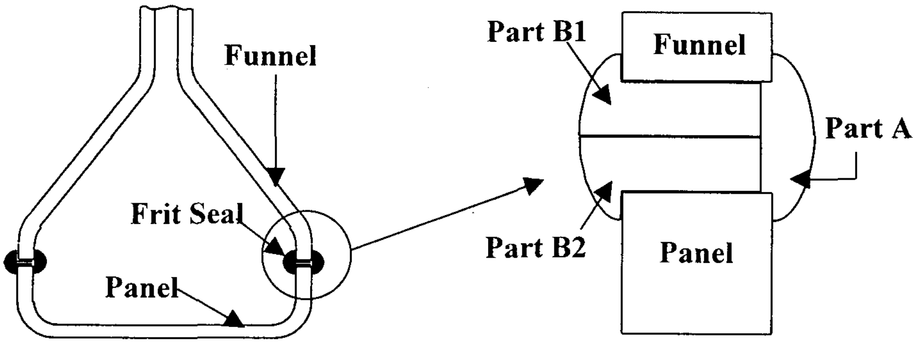

Fig. 1 The schematic drawing of CRT.

generation of HNO_3 mist and NOx gas. For this purpose, a new chemical is suggested. Its dissolution ability for lead and zinc oxides and its application to the separation of the CRT panel from the funnel are to be reported.

Experimental Procedure

The new chemical is a kind of acid called FST-100 (brand name). In this paper FST-100 is designated by HX.

Measurement of dissolution ability of 10% HX solution for PbO and ZnO powders

PbO or ZnO powders were put into 10% HX solution of 100 ml. The solution was stirred by a magnetic bar during 24 hrs and then was filtered. Then, the remaining PbO or ZnO in the form of solid were weighed. From the above, the dissolved amount was measured and then was compared with a theoretical value.

Separation of CRTs

Figure 1 shows the schematic drawing of a CRT including the panel, the funnel, and the frit seal. The part of frit seal is magnified. The part A seen in Fig. 1 was firstly removed by an injection of solution at the part A (Fig. 2(a)) or an irradiation of ultrasonic wave (Fig. 2(b)).

When the part A was removed, the alternating flows of hot water and cold water were supplied. This alternative supply provides the different thermal expansion which destroys the bond between the funnel and the panel, so that they can be separated each other. When separated, the frit was remained on both sides of the panel and the funnel as shown in Fig. 2(c).

In order to evaluate the separation effect, the time required to remove part A was measured. After removal of the part A, the panel and the funnel can be easily separated each other. Separation effect of HX solution was checked by the following variables; the method to apply the solution to the frit part (the injection or the use of ultrasonic wave), the concentration of HX solution, and the temperature of solution. The obtained results were compared with those obtained from the use of the nitric acid.

After separation between the panel and the funnel, the time required to remove the remaining frit parts, B1 and B2 was also measured. The complete removal of the remaining frit parts is a prerequisite to recycle and salvage the panel glass and the funnel glass separately, because the panel and the funnel contain different lead contents.

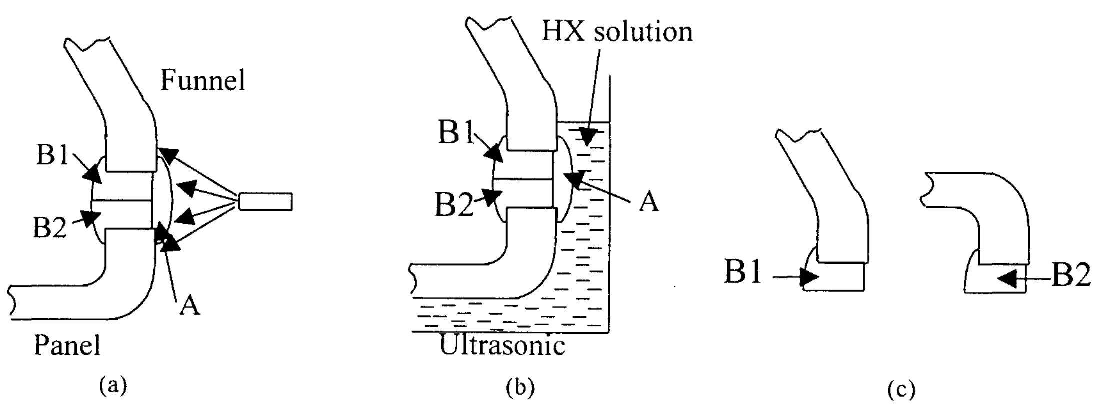

Fig. 2 The separation of the CRT by an injection (a) and a ultrasonic irradiation (b) and the frit remained after separation.

Results and Discussion

Dissolution Ability

Reaction of PbO and ZnO with the chemical HX can be presented by the following equations;

$$PbO + 2HX = PbX_2 + H_2O \quad (1)$$
$$ZnO + 2HX = ZnX_2 + H_2O \quad (2)$$

where, PbX_2 and ZnX_2 are reaction products. The solubility of PbX_2 at 25°C in water is 218 g/ 100 g and the solubility of ZnX_2 115 g/100 g. Firstly, PbO powders were reacted with 10% HX solution of 100 ml at the room temperature for 24 hrs. After filtration, the amount of remaining solid PbO powders was measured. Based on eq. (1), the dissolution amount was calculated to be 98.5% of the theoretical value. In case of ZnO powders, about 99% of the theoretical value was observed to be dissolved into the HX solution. These indicate that PbO and ZnO can be dissolved into the HX solution up to the stoichiometry limit.

Separation of the panel from the funnel

Figure 3 shows the time required for removing the frit A seen in Fig. 1 by the solution injection method. It is clearly shown that the use of the new chemical can reduce the removing time of the frit A, comparing with the use of 15% nitric acid. Increase in the solution temperature reduces the removing time. The effect of temperature is strong in case of the use of the nitric acid. Increase in the temperature by 20°C from 25°C to 45°C reduces the removing time from 5 to 3 minutes. However, the use of the new chemical is little dependent on the temperature.

Figure 4 shows results obtained by the ultrasonic irradiation. The trend is very similar to that observed by the solution injection method. However, the removing time is more reduced by the ultrasonic irradiation. This would be attributed to the fact that application of ultrasonic vibration enhances the diffusion of reactant to the frit and the removal of reaction products. In this kind of experiment, use of the nitric acid is strongly dependent on the temperature, whereas use of the new chemical is little dependent. Such a result indicates that the nitric acid should be used at high temperature of around 45°C, while the new chemical can be used even at the room temperature.

As mentioned above, after removing the part A, the alternative flow of hot water and cold water is applied to separate the funnel and panel parts. An example is in Fig. 5, showing that the panel part is clearly separated from the funnel part. From Fig. 5, we can extract another information on kinetics, because pictures in Fig. 5 were obtained by the following procedure. The sealing part on one side of the CRT was firstly immersed into the 10% HX solution under application of ultrasonic vibration and held for 5 minutes followed by extracted from the bath. Then, the second side was immersed and held for 8 minutes: 10 minutes for the third and 12 minutes for the fourth. From pictures magnified in Fig. 5, the removed amount of the frit between the panel and funnel sides can be calculated at a given time. The results are plotted in Fig. 6 as a function of time. The Y axis means the percentage of the removed amount to the amount of the frit existed between the panel and funnel sides. The removed amount is observed to be nearly proportional to the time.

Removal of remaining frit

Figure 7 and 8 show the time required for completely removing the frit B1 and B2 by the solution injection method and the ultrasonic irradiation, respectively. The use of the ultrasonic vibration is much more effective to remove the frit than the injected solution.

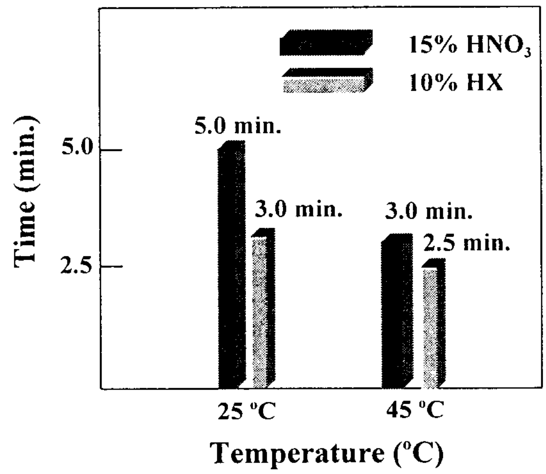

Fig. 3 The time required for the removal of the frit A as a function of solution temperature under the condition of the solution injection at the part A.

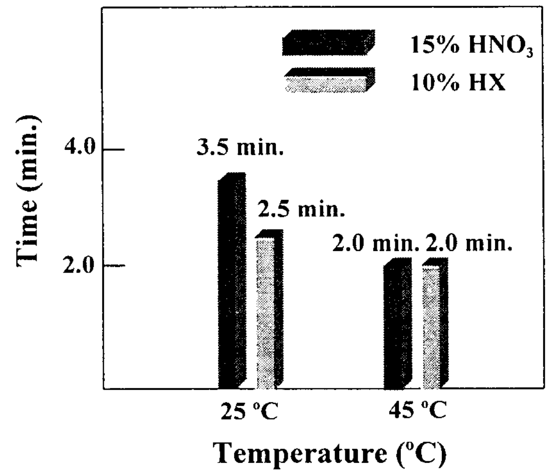

Fig. 4 The time required for the removal of the frit A as a function of solution temperature under the condition of the ultrasonic irradiation.

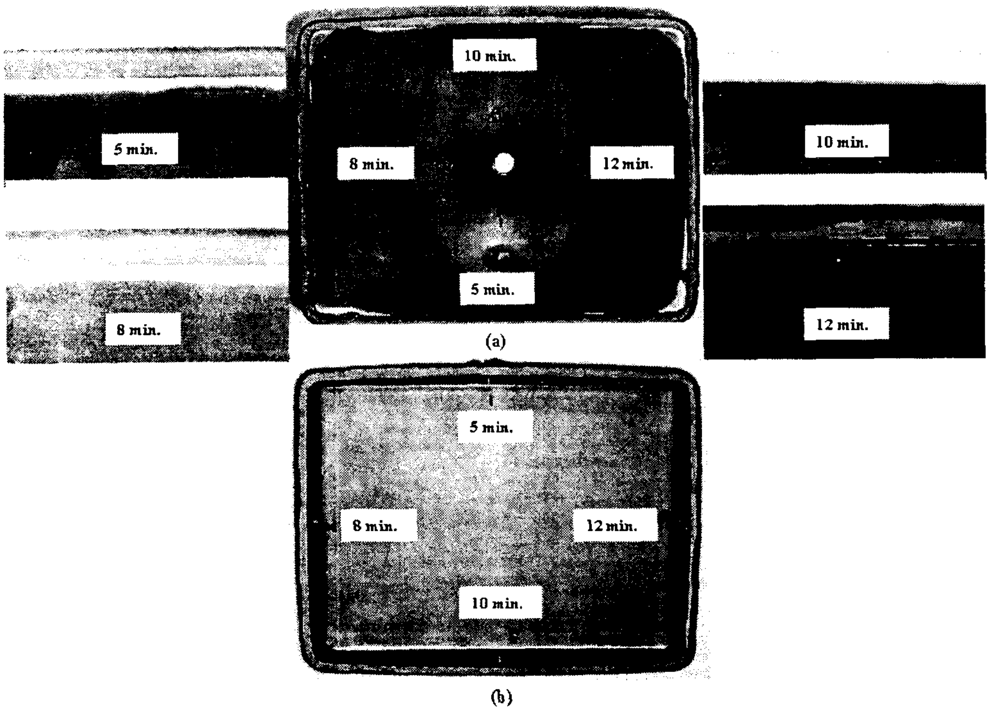

Fig. 5 The funnel part (a) and the panel part (b) separated by the alternative flow of hot and cold water (Before the separation, the CRT was immersed into the 10% HX solution by application of ultrasonic vibration).

In case of the use of nitric acid, the removing time of the frit B1 and B2 is strongly dependent on the solution temperature. Increase in the solution temperature by 20°C from 25°C to 45°C reduces the removing time up to about 50%; (a) 18 to 8 minutes for the solution injection and (b) 4 to 2 minutes for the ultrasonic irradiation. On the other hand, the use of new chemical is little dependent on temperature. These results are the same as those obtained for removing the frit A before separation of the panel and the funnel. Therefore, it is emphasized again that the new chemical can be used even at the room temperature, whereas the nitric acid should be used at high temperature of around 45°C.

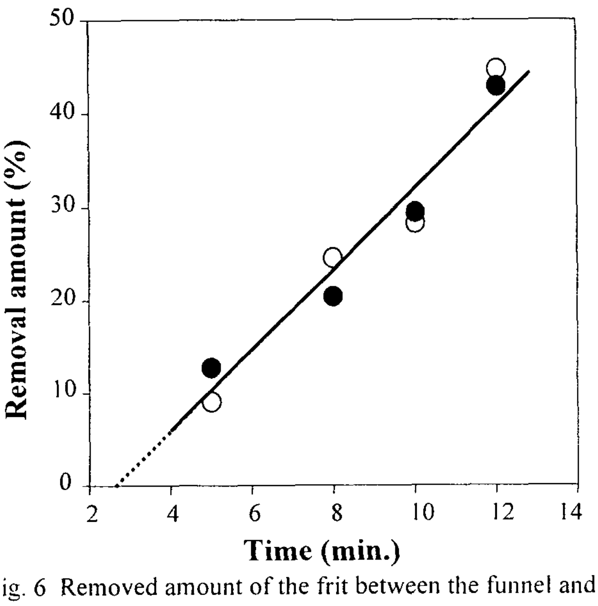

Fig. 6 Removed amount of the frit between the funnel and panel sides as a function of time at room temperature.

Effect of HX concentration

Figure 9 shows the time required for the complete removal of the frit B1 and B2 as a function of solution concentration at 45°C by the solution injection method. In case of the use of nitric acid, the time is strongly dependent on its concentration. Increase in the nitric acid concentration up to 15% reduces the removal time, but further increase to 20% increases the removal time again. This indicates that the control of nitric acid concentration is important. In fact, a CRT making industry controls the nitric acid concentration in the range of 12 to 17%. However, the concentration dependence of new chemical is negligibly small. This means that the new chemical is

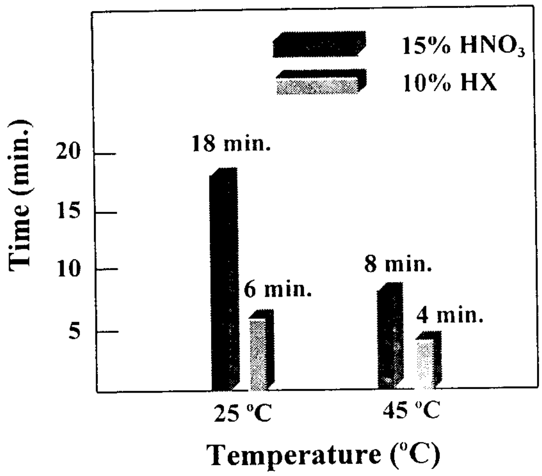

Fig. 7 The time required for the complete removal of the frit B1 and B2 as a function of solution temperature by the solution injection method.

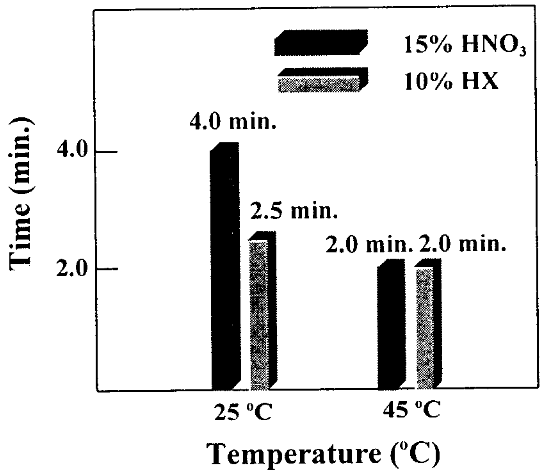

Fig. 8 The time required for the complete removal of the frit B1 and B2 as a function of solution temperature by the ultrasonic irradiation.

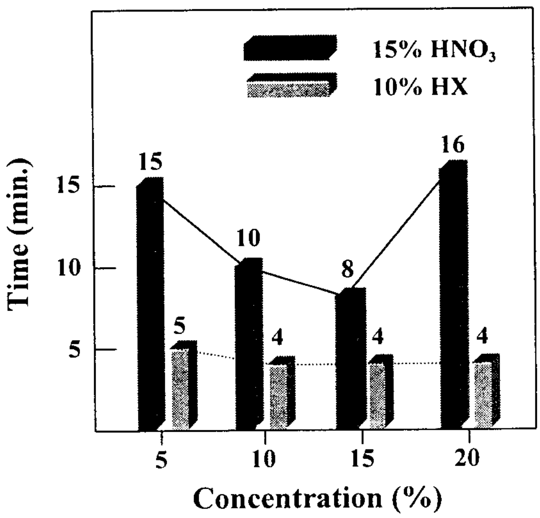

Fig. 9 The time required for the complete removal of the frit B1 and B2 as a function of solution concentration at 45°C by the solution injection method.

easily used without any special attention to control the solution concentration.

Summary and Conclusions

When compared with the use of nitric acid, the new chemical has the following advantages:

- No generation of HNO_3 mist and NOx gas,
- Improvement of working conditions,
- Operation at room temperature without any special attention for controlling the solution concentration, and
- Increase in productivity.

When compared with physical separation processes, the new chemical has an advantage of removing the frit completely without dust generation, so that the panel glass and the funnel glass can be collected separately. Thus, the lead concentration in landfill leachate can be minimized and the glass composition can be more easily controlled when returned to the glass making industries as raw materials.

In addition, this method can be applied to salvage CRTs in CRT-making industries for replacing the method using the nitric acid.

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