CRT GLASS AS SECONDARY RAW MATERIAL FOR CERAMIC GLAZES

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1. INTRODUCTION

A recent problem, which industrialized countries have only just began to deal with, is the management of waste (14 Kg/ inhab.year) coming from electrical and electronic equipment (WEEE), consisting mainly of television sets and computers containing cathode ray tubes (CRT). The recycling techniques for metals, plastics, and the electronic components already exist, while the utilization of CRT glass is quite problematical due to the different composition of the glasses. This is due to the fact that CRTs are normally made of several glass components divided into four typologies: 1) Panel (the front part): a very homogeneous barium strontium glass; 2) Cone (the hidden part inside the TV set): a lead glass; 3) Frit (the connection between the panel and the cone): a low melting temperature lead glaze; 4) Neck: a glass with a very high lead content enveloping the electron gun [1, 2].

Actually there is the possibility of usage the two main glasses in both closed-loop recycling (obtainment of new cathode ray tubes) and open-loop recycling (use of CRT glass into another productive cycle). Normally for the manufacture of new CRTs, the two glass fractions (the lead and the unleaded glass) are accurately separated and cleaned. The recycling in the melting batch has been estimated up to 30% for cone and 10 wt% for panel. The use of these glasses, in closed-loop recycling is destined to decrease with the advent of the new technologies as LCD and PDP and in a few years the production sites will shift to low developed countries.

On the other hand, open-loop recycling is not easy, because it is forbidden to introduce dangerous elements (such as lead, arsenic, cadmium) into products like glass containers, tableware or glass fibres. In this context, the glass industry is an excellent potential consumer only for glasses from the screens [3]. However, in the ceramic industry the chemical limitations are less restrictive and both main CRT glass are potentially acceptable as secondary raw material even if they must be supplied with particular characteristics of homogeneity, cleanness, etc. In this context our paper reports a research developed with the aim to use the CRT glass as secondary raw material in the formulation of glazes for porcelain stoneware and single–firing tiles.

2. RESULTS AND DISCUSSION

The CRT glass could be considered as a substitute for ceramic frits, because it contains barium, strontium, zirconium and lead oxides, which represent components that are often added to glazes in order to obtain specific properties (brightness, chemical resistance, matt effect, etc) (Table 1). Besides, from the economic point of view it represents an important raw material that allows reducing energy consumption and shortening production times.

Oxide	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	BaO	SrO	Fe_2O_3	Sb_2O_3	CoO	TiO_2	ZrO_2	ZnO	PbO	NiO	Others	total
Panel	61.23	2.56	8.27	5.56	1.13	0.76	2.02	8.84	0.10	0.30	0.02	0.35	0.91	0.18	0.02	0.03	-	100
Cone	56.72	3.42	6.99	5.37	3.12	2.02	4.03	1.99	0.11	0.30	0.00	0.19	0.24	0.22	15.58	0.02	-	100

Table 1. Chemical analysis (oxide wt%) for colour CRT glasses

For the study, two categories of CRT glass have been investigated: screen glass (TV + PC) colour, cone glass (TV + PC) colour. The thermal characterization of the analysed glasses has shown the low melting nature, corresponding to a low softening temperature (Ts) (855°C panel ; 750°C cone), and the high values (α: 9-10 x 10^{-6} °C^{-1}) of the thermal expansion coefficient. These results are in agreement with the relevant quantities of alkaline oxides present in the glassy network which confer low nature to the glass transition temperature (T_g) determined by DTA analysis (535°C panel; 505°C cone). The measurements of density confirmed the chemical analysis, showing higher density for cone glass (2.96 g /cm^3) with respect to the panel glass (2.74 g /cm^3). This fact is due to the high atomic weight of the lead present in the cone composition. From the characterization results, the research has been directed towards the obtainment of single-firing ceramic glazes at semi industrial scale in a ceramic factory. Different amounts of panel glass (14-35 wt% ranging) as substitutes of "ceramic frits" were prepared mixed with other ceramic components. These tests were carried to the determination of a quantitative limit of glass to introduce (30 wt%) without generate aesthetical defects and avoiding the problem related to the high α value (crazing defect). The re-modulation of the raw materials ratios was necessary to obtain a glaze α coefficient (6.6 x 10^{-6} °C^{-1}) similar to the support one (tolerance admissible 1 x 10^{-6} C^{-1}). From the rheological tests, it is possible to confirm that glaze suspensions are non Newtonian systems [4]. The flow curve obtained shows a low yield stress (0.131 Pa) and an elevated viscosity value at lower shear rates and a linear trend at higher shear rates (>100s^{-1}) typical of Plastic Bingham behaviour. Besides, it is possible to observe a small hysteresis between flow up and flow down curves that indicates the stability of the glaze suspension (absence of settling process). The on-off and single step tests results are in agreement and permit to identify a thixotropic behaviour for these suspensions. In fact the viscosity decreases as a function of time under constant shear rate (200 s^{-1}) (Figure 1). The base glaze suspension was applied on the green ceramic body in order to obtain three different aesthetic decorations: red marble for single firing, and rustic and metallised for porcelain stoneware tiles. After firing on these samples the tests according the ISO norms relating to glazed ceramic tiles were conducted. The results of the chemical resistance tests allowed observing that there are no appreciable differences between the samples containing CRT glass and standard industrial glazes. The staining tests results showed a high resistance to dirt for all samples, class 5 as the standard (the stains are removed using only water). Besides, the resistance to surface abrasion tests point out that the introduction of CRT glass into the formulation of glazes improved the abrasion resistance of the Metallised type (from class 3 to class 4) and confirmed the values of the standard product for the Rustic (class 4) and Red marble (class 3) types. The products containing CRT glass do not present visually perceptible differences with respect to the originals; notwithstanding this, CIELab colorimetric analysis was applied in order to perform a scientific evaluation. The performed tests show ΔE* values in the range 1,6-4,4, while the tolerance for a ceramic products is 1. This behaviour is related to both the absence of boron, which has a strong colour fixing capacity, in the CRT glass with respect to commercial frits and to the presence of Sr, Ba and Pb, which can interact with the chromophore ions giving colour alterations. It is important to note that the products containing CRT glass do not present significant differences in the technological properties with respect to the originals, so that these glasses can be exploited to produce pigmented, silk-screened and flame-hardened products.

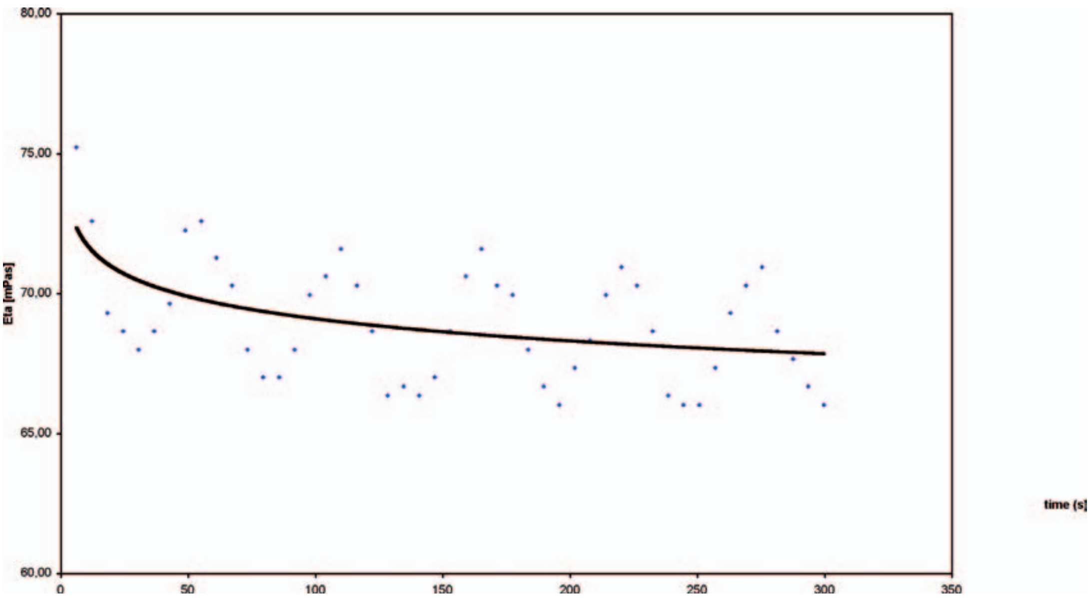

Figure 1.

3. CONCLUSIONS

From the results obtained it is possible to note that CRT glass from old TVs and PCs could be recovered in a new open–loop recycling avoiding disposal in landfill. The glazed surfaces prepared using 30 wt% of CRT panel glass in the formulation do not present technical differences with respect to the standard. The study performed showed the possibility of CRT glass reuse as a secondary raw material for the ceramic glazes production with good aesthetical and technical characteristics of final products and with a reduction of the environmental impact.

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