

## CRT glass state of the art A case study: Recycling in ceramic glazes

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### Abstract

The management of electrical and electronic equipment waste (WEEE) is a significant problem of industrialized countries, in the last decades it has been noticed an appreciable increase of this residue, consisting of about 80% of television sets and computers containing end of life (EOL) cathode ray tubes (CRT). Specific technologies permit to dismantle the kinescope, obtaining different glasses with high quality level and specific chemical compositions. The presence of dangerous elements makes critical the re-use in many fields of application. The present work proposes the feasibility of CRT glass recycling in ceramic field using it into a base glaze formulation as substitute of “ceramic frits”. The study was conducted in two phases, laboratory scale in order to study the suitable glaze formulation and semi-industrial scale with the technological support of an Italian ceramic glaze producer. The glazes obtained have aesthetic and mechanical properties extremely similar to the standard ones.

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**Keyword:** Traditional ceramics; Glass

### 1. Introduction

Nowadays the electric and electronic equipment (EEE) occupy a very relevant place both in the domestic life and in the working and productive activities.

This category includes, the equipments whose operation depends just from electric currents or electromagnetic fields: the large household (refrigerators, freezers, washing machines, dishwashers, ovens, etc.); the small household (vacuum, toasters, wakes up, razors, etc.); the telecommunications and information technology equipments (pcs, printers, copiers, fax, cells, etc.); the equipment of consumption (radios, TVs, video cameras, etc.); the equipment of illumination (fluorescent lamps and tubes, incandescent lamps, etc.); the electric and electronic tools (drills, saws, sewing machines, etc); the toys and the equipments for free time and sport (electric trains, video games, etc.); medical dispositives (equipments for radiotherapy, cardiology, dialysis, etc.).<sup>1</sup> Their production needs an enormous quantity of raw materials, whose extraction and transformation represent an important source of environmental damage. The fall of the prices combined to the anti-economical reparations accelerate

the process of EEE substitution. In Europe are produced annually 7.5 million tonnes of waste of electrical and electronic equipment (WEEE), that corresponds to 4% of the urban solid waste flow, and it has been estimated that the growth trend will rise at 3–5% for year. This trend represents a growth three times faster than of the average municipal waste.<sup>2,3</sup> Latest estimates indicate that the EU produces an average of 14 kg/WEEE/inhabitant/year. Because of the dangerous substances contained into the WEEE (PCB, halogenate substances, heavy metals, etc.), both the incineration process and the landfill represent a risk for the environment and the human health. For this reason, industrial activities of dismantling of end of life (EOL) electronic goods, have been initiated in Europe in order to avoid the final disposal. These technologies allow the recovery and recycle of the various components, obtaining different kind of materials (plastics, rubbers, electronic circuits, metals and glasses), some of them are ready to use, others need a claiming step before their use as secondary raw materials. In particular, the treatments carried out upon television sets and computer monitors permit the separation of the cathode ray tube (CRT) that is two thirds of the entire weight of these apparatus and consists for 85% of glass. Colour CRTs generally are composed by four different glasses, each one having a particular chemical composition, very different from the others.

In the last years in the EU, particular attention has been focalized to the WEEE as it appears by considering the develop-

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ment of a specific legislation. These directives shall come into force and modify Member States companies behaviour. Directive 2002/95/CE regarding restrictions of the use of hazardous substances in electrical and electronic equipment (ROHS): (1) implements the principle for producers to take into account the limit to use of hazardous substances at the product design step; (2) imposes a restriction to the use of hazardous substances in the manufacture of EEE, encouraging the alternative use of secure substances for the human health and the environment; (3) advises the development of the research on the substitution products. Directive 2002/96/CE regarding the recyclability of WEEE: (1) incorporates the responsibility principle, imposing to the producer to take responsibility for the environmental impacts that their products may have during all their life cycles; (2) encourages the planning/production of EEE that facilitate the recovery of their components and materials; (3) establishes different percentages of recovery and recycling as a function of the product category; (4) adopts measures to minimize the digestion of WEEE as urban waste in order to reach a high level of differential collection from domestic units (4 kg/inhabitant/year). These decisions will increase challenges to find out possible re-uses for EOL CRT glass, the main component of TV sets and PC monitors.

This paper reports the chemical compositions and properties required for CRT glass, presents an overview through bibliographic research on the European current status of the recycling for CRT glass and analyses the possibilities of closed and open loop applications. Besides, it discusses a research project developed at the Modena and Reggio Emilia University, exploring open loop recycling feasibility in the ceramic field. The aim of the work is oriented to use the CRT glass as secondary raw material as substitutes for common “ceramic frits” in the formulation of commercial glazes.

## 2. Technical characteristic of cathode ray tube from TV and PC

It is estimated that approximately 65% of the weight of a television set or a computer monitor is constituted of cathode ray tube (CRT) or kinescope, and it is composed for 85% of glass (65% panel and 30% funnel and 5% neck glass).

Monochrome CRT consists of three parts: a panel glass used as screen, a neck glass, in which an electron gun is inserted and a back funnel glass that connects the panel and the neck (Fig. 1). The panel and funnel glass are formed by pressing individually and later they are sealed together without a junction.<sup>4</sup>

The colour CRT structure is essentially similar to the monochrome one with some technical differences. The base is the monitor’s “screen” that is coated on the inside with a matrix of thousands of tiny phosphor dots. Phosphors are chemicals which emit light when excited by a stream of electrons: different phosphors emit different coloured light. Each dot consists of three blobs of coloured phosphor: one red, one green, one blue. These groups of three phosphors make up what is known as a single pixel.<sup>5</sup> In the neck there are three electron guns for the red, blue and green. Three electron beams from each electron gun pass through a hole in the shadow mask and excite phosphor

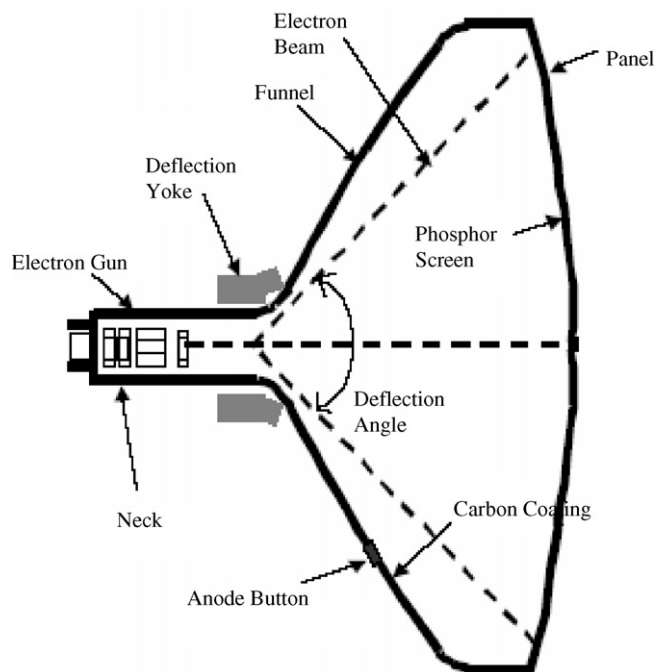
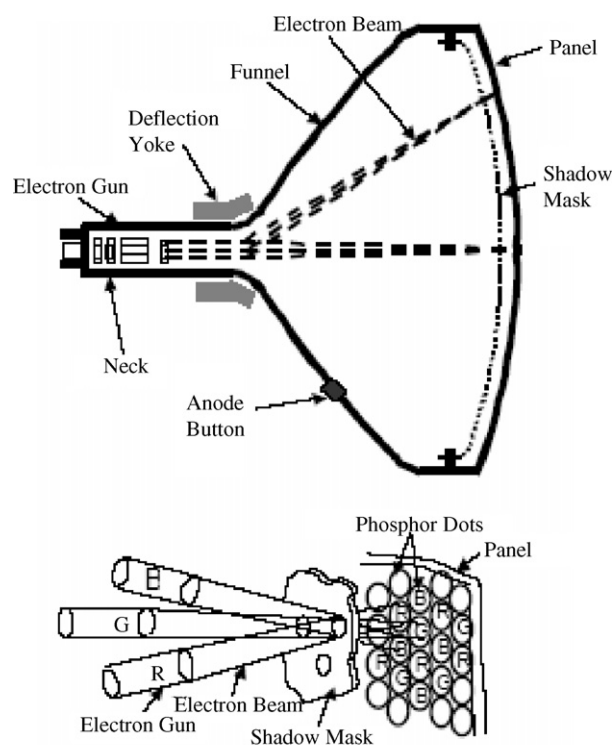


Fig. 1. Structure of monochrome kinescope.

coating on the inside of the panel (Fig. 2). The shadow mask is a steel panel with a mask that forms a pattern on the screen. Panel glass after coating is sealed to the funnel glass with a lead frit as junction. There is another kind of colour CRT system which



Relative Position of Electron Gun, Shadow Mask and Phosphor Screen

Fig. 2. Structure of colour kinescope.

uses vertical wires under tension, an aperture grill instead of a shadow mask (Triniton system).<sup>4</sup>

### 3. Compositions and characteristics of CRT glasses

The main properties required for CRT glasses are X-ray absorption, electric resistivity and a thermal expansion suitable to the other glass parts and sealing metal. High light transmittance is also important for the panel glass to display clear pictures. In addition, it is essential that light transmittance is not deteriorated by electron beam or X-ray irradiation. Different kind of glasses for each part of black and white (B&W) and colour CRTs are used according to their technical specifications:

1. Panel (screen, the front part): a very homogeneous barium–strontium glass, of a greenish-blue colour, whose weight is about two-third of the whole CRT;
2. Cone (the hidden part inside the TV set): a lead glass, whose weight is about one-third of the whole CRT;
3. Neck: a glass with a very high lead content enveloping the electron gun;
4. Frit (the junction between the panel and the cone): a low melting lead glass, included only in colour CRTs.

From the chemical analysis of glass coming from B&W equipments, no substantial differences were shown in the composition for panel and funnel. Barium oxide (11 wt.%) is present in order to avoid radiation exposure, the lead oxide is normally absent. On the contrary, high lead content is observed into neck glass. All the three glasses analysed contain relevant quantities of alkaline oxides (13–15 wt.%) that notably influence their properties<sup>6</sup> (Table 1). The presence of lead oxide is associated to the X-ray shielding ability required for the glass to prevent the dispersion. The shielding ability is evaluated by X-ray absorption coefficient at the 0.06 nm wavelength. This

Table 1  
Chemical analysis (oxide wt.%) of black and white CRT glasses

Oxide	TV + PC panel	TV + PC funnel	Neck
SiO <sub>2</sub>	66.05	65.49	56.50
Al <sub>2</sub> O <sub>3</sub>	4.36	4.38	1.00
Na <sub>2</sub> O	7.63	7.05	4.00
K <sub>2</sub> O	6.65	5.72	9.00
CaO	0.00	0.00	0.00
MgO	0.01	0.00	0.00
BaO	11.38	11.20	0.00
SrO	0.99	0.94	0.00
Sb <sub>2</sub> O <sub>3</sub>	0.44	0.44	0.40
Fe <sub>2</sub> O <sub>3</sub>	0.25	0.14	0.00
CoO	0.01	0.01	0.00
TiO <sub>2</sub>	0.13	0.03	0.00
ZrO <sub>2</sub>	0.07	0.01	0.00
ZnO	0.00	0.00	0.00
PbO	0.03	0.00	29.00
NiO	0.04	0.03	0.00
Others	1.96	3.56	0.00
Total	100	100	100

Table 2

Chemical analysis (oxide wt.%) of colour CRT glasses

Oxide	TV + PC panel	TV + PC funnel	Neck
SiO <sub>2</sub>	61.23	56.72	50.00
Al <sub>2</sub> O <sub>3</sub>	2.56	3.42	1.00
Na <sub>2</sub> O	8.27	6.99	2.00
K <sub>2</sub> O	5.56	5.37	10.00
CaO	1.13	3.12	2.00
MgO	0.76	2.02	0.00
BaO	10.03	4.03	0.00
SrO	8.84	1.99	0.00
Fe <sub>2</sub> O <sub>3</sub>	0.10	0.11	0.00
Sb <sub>2</sub> O <sub>3</sub>	0.30	0.30	0.30
CoO	0.02	0.00	0.00
TiO <sub>2</sub>	0.35	0.19	0.00
ZrO <sub>2</sub>	0.91	0.24	0.00
ZnO	0.18	0.22	0.00
PbO	0.02	15.58	34.00
NiO	0.03	0.02	0.00
Total	100	100	100

coefficient derives from the density of glass and the integration of the mass absorption coefficient of each metal oxide contained in glass. Lead oxide has the largest mass absorption coefficient among the other oxides contained in the composition. For B&W CRTs the X-ray absorption coefficient for panel and funnel is about 23 and for the neck is about 82.<sup>7</sup>

The CRT glass coming from colour equipments, presents important differences in composition between panel (screen) and funnel (cone). The screen is characterized by high levels of BaO (9–11 wt.%) and SrO (8–10 wt.%), the cone instead contains a significant quantity of PbO (18–20 wt.%) that is moreover completely absent in the panel<sup>6</sup> (Table 2). The reason of the different chemical composition derives from the technical evolution. In the last 25 years the colour CRT glass properties have been evolved, in particular concerning the improvement in brightness and contrast. The colour CRT are become more than 10 times brighter than the first models and 2 times than the B&W equipments. The increase of the accelerating voltage has provoked the need of raising the contents in the glass composition of the elements with high X-ray absorption ability. In the case of funnel and neck glass, PbO oxide content was increased, but the same measure was not possible for panel glass, because of the browning phenomenon. The accelerating voltage in colour CRT varies from 20 to 30 kV and in the B&W equipment from 10 to 20 kV. For this reason the former needs a higher X-ray absorption ability than the monochrome one.<sup>4</sup> The X-ray absorption coefficient for panel, funnel and neck of colour CRTs are 29, 66, 100, respectively.<sup>7</sup> The increase of accelerating voltage intensifies the electron beam that irradiates in a specific place of the screen, resulting the browning effect on the panel glass. This phenomenon is caused by a reduction of metal ions in the glass by electron beams and the generation of metal colloids. Lead ion is the easiest metal ion to be reduced in glass as a result in browning acceleration caused by the generation of lead colloids. Consequently, lead oxide has been removed from the panel compositions, while initially they contained from 0.5 to 3 wt.% lead oxide.<sup>4</sup> The X-ray absorption is

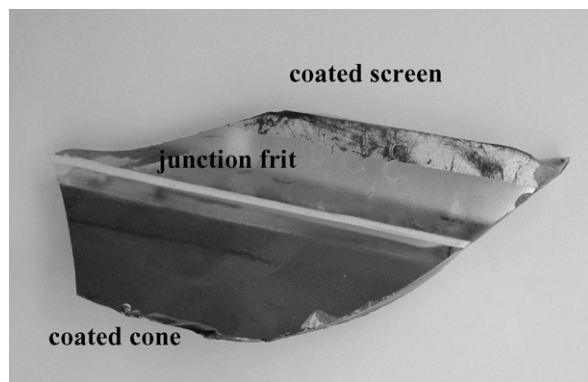


Fig. 3. Appearance of CRT glass before treatment.

maintained by adding higher amounts of barium, strontium and zirconium.

The browning occurs even in leadless glass because alkali ions such as sodium are reduced and generate the brown colour. Therefore, it is common in the panel glass composition to find more than two kinds of alkali oxides in order to prevent the colouring. The ratio of sodium and potassium is optimized and the amounts of both are almost equal. The presence in the composition of small amounts of cerium has the effect of preventing the X-ray browning, the antimony is present as fining agent to refine the melt avoiding the bubbles in the glass. Besides, the addition of titanium to glass ingredients has the effect to prevent solarization (effect of sunlight). The panel glass are tinted with cobalt and nickel oxides in order to give the correct light transmission. The panel and funnel glass are coated with different kind of substances that contain heavy metals and hazardous elements. Some authors describe the presence of four coating layers into the inner surface of the panel glass. In the first coating layer a mixture of carbon slurry and other surfactants produces a carbon black and clear stripes; three fluorescent colour powders (green, blue and red) form the second layer. The third is a lacquer (a wike like layer) applied to smooth and seal the fluorescent powders into the inner surface of panel glass. The final coating is an aluminium film used to enhance the brightness. On the other hand, for the cone only two coatings are identified: one a non-reflective black graphite (rich in iron oxide) into the inner surface and the other an external carbon black paint.<sup>8</sup> In Fig. 3 is showed a part of kinescope before treatment and it is possible to note the two main CRT glass with the coatings (screen and cone) and the frit junction.

#### 4. Status of the recycling (closed- and open-loop cycle)

In the latest years the EU Member States have been occupied to the WEEE problematic. The recycling techniques for metals, plastics, and the electronic components already exist, while the utilization of (EOL) CRT glass is quite problematical due to the different composition of the glasses above described. In order to solve this problem, from 1997 to 2000, the Recytube Project, financed by the European Community, set up a technology able to produce economically a high-quality secondary raw material (SRM) from the processing of (EOL) CRT glass.<sup>9</sup>

With this SRM, both closed-loop recycling, i.e. the usage of CRT glass in further obtainment of cathode ray tubes, and open-loop recycling, i.e. waste CRT glass being recycled into another productive cycle, can be performed.

Normally for the manufacture of new CRTs, the two glass fractions (the leaded and the unleaded glass) are accurately separated and cleaned. An important step towards a closed loop recycling was taken when the most important European CRT producers (Schott, Philips, Samsung, Thompson and NEG) reached an agreement on the composition of funnel glass and was decided a specification for the panel cullet (regarding lead content) aimed to facilitating the increase of recycling quota. Actually the recycling of clean cone and panel glass in the melting batch has been estimated up to 30 and 10 wt.%, respectively. The usage of the two main glasses in closed-loop recycling is destined to decrease and in the future the panels production will be moved in the West Europe countries (Schott). The event of the new LCD and PDP technologies will allow in few years (within 2010) the shift of production sites to emerging countries as India, China and Southeast Asia. From these considerations it is possible to hypothesize a drastic reduction of the close-loop recycling.

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 without the above-mentioned elements, such as carefully selected glass from the screens. In the ceramic industry the restriction is not so restrictive and both glass from screens and cones are potentially acceptable as secondary raw material even if they must be supplied with particular characteristics of homogeneity, cleanness, etc.

Some EU experiences of open-loop recycling are below described:

- *Potential use in brick manufacturing*: Staffordshire University (UK) has developed, and is currently patenting, a process using container cullet and panel glass waste as a flux agents in the manufacturing process with a save of energy. The process requires ground glass to obtain particle size between 0.5 and 1 mm that is then pressed in a mould with a binder. The tests carried out on fired samples highlighted good results from chemical, physical and mechanical properties but not enough to satisfy the engineering brick requirements. The products obtained will be use as decorative products in building or highways.<sup>10</sup>
- *Potential use in foam glass*: Foam glass is already manufactured from waste glass on a commercial scale, manufactures have confirmed that there are no known technical barriers to use waste CRT glass. The product obtained would be marketed as loose fill aggregate replacement for concrete products. Based to different companies' experience, as Hasopor's (Norway) and Misapor (Suisse), it should be technically feasible to include up to 20% CRT panel in foam glass formulation. The results were promising but they are not yet transferred into a market reality.<sup>10</sup>



In Italy different research groups are working about the possibility to use CRT glass in ceramic manufacturing:

- *Use of CRT glass in tableware glass production:* Stazione Sperimentale del Vetro -SSV (Murano, Italy) has developed a study in order to produce coloured tableware glass using into the batch a 97 wt.% of panel glass waste. The tests were performed in a full scale in collaboration with a glass factory (EFFETRE INTERNATIONAL Comp., Venice). The kind of glass obtained from the melting process (1300 °C) was a good fumè glass with some small seeds which did not compromise its quality. The leaching tests were positive considering that not toxic elements occurred. Many articles as glasses, plates, cups, etc. were produced.<sup>11</sup>
- *Use of CRT glass in insulating glass fibre production:* The SSV in the framework of Recytube project has developed a research relative to the production of fibre glass by adding about 10 wt.% of panel glass to a typical batch composition for commercial A glass fibre. The quality of the fibres obtained was quite comparable to the original ones. Although the tests conducted at laboratory scale were promising, the fibre manufacturers are reluctant to use CRT panel glass on industrial scale, due to the possible dangerous effect on health derived from the presence of Ba and Sr contents in the glass.<sup>11</sup>
- *Use of CRT glass on ceramic bodies:* Two different researches were performed by ISTECC-CNR (Faenza) and Modena University in order to verify the possibility of introducing CRT glass in porcelain stoneware bodies. The tests carried out in laboratory scale show that percentages up to 5 wt.% of CRT glass (panel and funnel glass) do not modify the requirements of final products. Although the use of cullet glass in ceramic industry as fluxing agent has a wide spread, the introduction of CRT glass is not still applied.

Although scrap CRT glass can be remoulded to obtain glass and ceramic products, the recycling market is not well-established worldwide. The lack of a recycling market may be due to the following reasons:

- Actually only panel glass has a concrete possibility derived from the research to be reused in other productive cycles; however the presence of barium and strontium into the panel glass is not well accepted in the fibre market even if experimental results are encouraging.
- The current legislation imposes a restriction to the use of lead containing materials as funnel glass in order to avoid a risk for the environment and the human health.
- The coatings adhering to CRT glass hinder the recycling. The fluorescent powder coatings, which contain hazardous elements (Cd, P, etc.), poses a negative effect to the recycler and the environment. Organic coatings (graphite) are unwanted substances in the glass manufacturing industry since they interfere with the glass melting process and they cause a low quality glass product. For this reason it is very important the development of new technologies in order to claim the CRT glass for their safe use as secondary raw materials.

- There are many difficulties to transfer the results of the applied research to the productive sector because of economical aspects are preferred with respect to environmental ones.

## 5. Use of CRT glass on ceramic glazes (a case study of Modena and Reggio E. University)

Glaze suspensions are composed of different types of raw materials, which can be divided into three groups: non-plastics, plastics and additives. The non-plastic materials include oxides, pigments, feldspars and others principal components such as frits. The frits are obtained from mixtures of silicates and carbonates which are melted and rapidly cooled in water. Plastic materials are clays, generally kaolin and bentonite. Finally, the additives used to optimize the glazing process are dispersing, deflocculating, binders and defoaming agents.<sup>12</sup> As regards glazing manufacturing, (EOL)CRT glass could be considered as a substitute for non-plastic materials, in particular ceramic frits. Moreover, 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.). Thus, CRT cleaned glass could represent an important raw material able to help to reduce the energy consumption and to shorten production times. This idea derives from the generally accepted concept for which the use of recycled materials is environmentally preferable to that of virgin raw materials.

For the study conducted in laboratory scale three categories of CRT glass has been investigated in order to study a suitable glaze formulation: screen glass (TV + PC) colour, cone glass (TV + PC) colour and mixed (screen + cone) black and white. The thermal properties characterization carried out by the hot stage microscopy and the thermo-dilatometric analysis of all analysed glasses have shown the low melting nature, corresponding to a low softening temperature ( $T_s$ ), and the high values of the thermal expansion coefficient ( $\alpha$ ). These results are in agreement with the relevant quantities of alkaline oxides contained in the glassy network. The low melting nature is also related to the glass transition temperature ( $T_g$ ) determined by DTA analysis (Table 3). The measurements of density carried out on CRT glasses have substantially confirmed the results of the chemical analysis, showing the same density values for panel and cone coming from B&W equipment (2.60 g/cm<sup>3</sup>), and higher densities for cone glass coming from colour CRT (2.96 g/cm<sup>3</sup>) with respect to the panel (2.74 g/cm<sup>3</sup>). This is due to the presence of lead that has a high atomic weight.<sup>6</sup> After the characterization of the CRT glasses and the analysis of their properties, the

Table 3  
Thermal properties for colour (TV + PC) and B&W CRT glasses

Type of glass	Transition glass temperature, $T_g$ (°C)	Softening temperature, $T_s$ (°C)	Dilatometric coefficient, $\alpha$ ( $\times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ )
Colour panel	535	855	9.99
Colour funnel	505	750	9.79
B&W mixed	490	720	9.15

research has been directed towards the obtainment of double-firing ceramic glazes, because of the lower firing temperatures of the industrial cycle. For the laboratory tests different formulations using glass, kaolin and kaolinitic clay ranging in 80–95, 5 and 15–0 wt.%, respectively, were prepared. The enamels obtained were transparent due to both the higher amount of alkaline oxides and their tendency to not crystallize. All the compositions prepared after firing showed crazing defect; the presence of clay materials decreases the intensity of the defect but did not avoid it. The phenomenon is presented in the form of a thick reticulate of thin irregular cracks because the glaze dilatometric coefficient ( $9\text{--}10 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ) is higher than that of the support one ( $7.6 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ).<sup>13</sup> From the obtained results it is possible to note that slightly different characteristics (tone more dark for that containing panel) are shown if panel or funnel is used in the formulation. Besides, using the only CRT glass as vitreous fraction the glaze produced presents a low aesthetical properties (cracking and spot resistance). A re-modulation of the raw materials ratios was necessary to obtain a better agreement between glaze and support dilatometric coefficient. A new composition, obtained by mixing sodium feldspar, boric acid and CRT glass (20 wt.%) permits to obtain a boric rich frit characterized by a lower thermal expansion coefficient ( $8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ).

Starting from the satisfactory laboratory scale results, a public-private partnership has been formed by the Province of Reggio Emilia, the University of Modena and Reggio Emilia, and two companies that operate on the local territory: the first, a national leader in the sector of recovery and treatment of electrical and electronic waste and the latter an important Italian ceramic glaze producer. The semi-industrial scale activity has been carried out on the frame of a pilot project called “Feasibility study of recycling glass and plastic components from junked TV sets and PCs”. In this phase of the work only the panel glass was chosen for the experimentation due to the large amounts available. The glaze prepared compositions contain about 35% of vitreous fraction, part of which (more than 80 wt.%) was substituted by CRT glass. The identification of this limit percentage is related to the importance of avoiding defects such as bubbling, cracking, warping of the support, etc. Also in this phase appeared the problem related to the high  $\alpha$  value. Therefore, a little re-modulation of the raw materials ratios was necessary to obtain a glaze  $\alpha$  coefficient ( $6.6 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ) similar to the support one (tolerance admissible  $1 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ ) in order to avoid the crazing defect. Since the application step is the phase in which a ceramic industrial process is most conditioned by the rheological properties of the glaze itself, particular attention was focused on the viscosity study. The rheological characterization yields the flow curve from which useful parameters for controlling the suspension behaviour (apparent viscosity, yield stress, thixotropy) may be inferred. The glaze suspensions are non-Newtonian systems, i.e. the viscosity is not an absolute value at constant temperature and pressure. In these systems is more appropriate to define an apparent viscosity as a function of the shear rate and the measure time.<sup>14</sup> From the flow curve test performed on the base glaze (Fig. 4), it is possible to note a plastic behaviour highlights from both a low yield stress (0.131 Pa) and an elevated viscosity value (viscosity curve). At higher shear

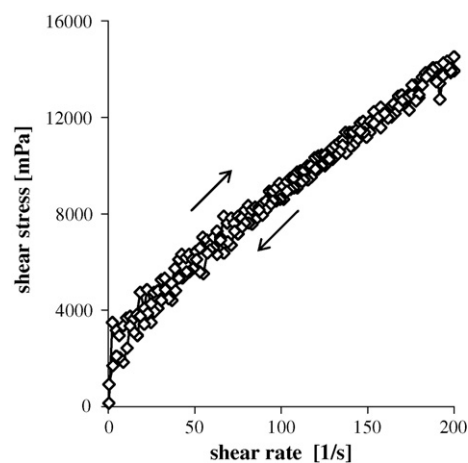


Fig. 4. Flow curve of CRT glaze suspension.

rates ( $>100 \text{ s}^{-1}$ ) the curve has a linear trend, 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 stability of the suspension is an important condition that guarantees a good application of the glaze on the tile surface. The results obtained from the time dependence study (on–off and single step tests) are in agreement and permit to identify a thixotropic behaviour for these suspensions. The base glaze was used to produce pigmented, silk-screened and flame-hardened products used industrially to glaze floor tiles by means of the overlapping of several layers. By applying these glazes on the green ceramic support, three different aesthetical decorations were prepared, red marble for single firing and rustic and metallized for porcelain stoneware tiles. All these products have been characterized by chemical resistance, staining and surface abrasion tests in accordance with ISO testing methods. From the aesthetical point of view colorimetric test by  $\text{CIEL} \times ab$  were performed.<sup>6,15</sup>

The results of the chemical resistance tests (UNI EN ISO 10545-13) allowed to observe that there are no appreciable differences between the samples containing CRT glass and standard industrial glazes, except for the rustic type where there is a worsening of the property regarding to acid attack resistance. The staining tests (UNI EN ISO 10545-14), performed with blue methylene and potassium permanganate ( $\text{KMnO}_4$ ), is an indirect evaluation of the open porosity of the glazed products considered after firing. These showed a high resistance to dirt; the belonging class is 5 (the stains are removed using only water) as the standard one. As regards to the resistance to surface abrasion tests (UNI EN ISO 10545-7), it was observed that the introduction of CRT glass into the formulation of glazes improved the resistance to abrasion of the Metallized type (from classes 3 to 4) and confirmed the values of the standard product for the Rustic (class 4) and Red marble (class 3) types.<sup>6,15</sup> The similar behaviour, in the above reported properties, between the standard and CRT based glazes is imputable to both the similar chemical composition and structure of the materials because the introduction of CRT panel glass does not vary the melt ability,

the viscosity and the capacity to form a glassy network of the glaze.

Parallel to the experimentation above illustrated, the production of 1 kg of two glazes (standard and with CRT glass in the formulation) was compared using the life cycle assessment (LCA) methodology.

The LCA (as standardized by the UNI EN ISO 14040-14043 regulations) is an instrument for evaluating the aspects and potential environmental impact associated with a product, a process or an activity throughout its entire life cycle (extraction and treatment of raw materials, manufacture, transport and distribution, re-use, usage, maintenance, recycling and disposal) and the consequent identification of opportunities for optimising and improving it for an environmental as well as economic and social point of view. SimaPro 5.0 software was used in the study and Eco-indicator 99 was chosen as evaluation method. This method considers three damage categories of potential environmental impact: “human health”, “ecosystem quality” and “resources”. Each damage category grouped several impact categories together. The results of the analysis showed that the production of glaze with CRT glass, with respect to standard glaze production, leads to a decrease of the overall potential damage of 36%. These results derives from the non-production of the frit, the decrease of the raw materials extraction and transport, the lower of NO<sub>x</sub> emissions and saving combustible.<sup>6</sup>

## 6. Conclusions

From the considerations summarized in the precedents paragraphs, linked to the chemical compositions, it is possible to say that the recycling of CRT glass is not simple because a cathode ray tube is composed of four different types of glass (panel, funnel, neck and frit junction). The problematic of CRT glass can be solved by two principal ways: closed- and open-loop recycling. Closed recycling is highly conditioned by both the distance of the CRTs production plants and the progressive substitution of traditional kinescopes for new technological products. These problems contribute to make necessary to identify alternative channels for the re-use.

The open-loop recycling will be the main way to manage this kind of residues notwithstanding the presence of dangerous elements, such as lead and other heavy metals, that forbids their recycling in the glass containers and glass fibre industry.

For both kind of loop recycling it is more important to reach international standards on the quality of EOL CRT glass to promote its re-use as precious resource not as waste.

Many different research groups in Europe are working on the open loop recycling with good experimental results. Among these, the University of Modena and Reggio E. is developing a pilot project to exploit these glasses in the ceramic field.

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