Sb₂O₃ Yerine CeO₂ Kullanımı İle Sofra Camı Eşyalarında Kalitenin Arttırılması

Recep KURTULUŞ¹, Veli UZ²
¹ Afyon Kocatepe Üniversitesi, B Materyal Bilimleri Fakültesi, Afyonkarahisar.
² Kütahya Dumlupınar Üniversitesi, B Metalurji ve Materyal Bilimleri Fakültesi, Kütahya.

e-posta: rkurtulus@aku.edu.tr ORCID-ID: 0000-0002-3206-9278
e-posta: veli.uz@dpu.edu.tr ORCID-ID:

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Öz

Anahtar kelimeler
Cam; CeO₂; Sb₂O₃; Sofra Eşyası.

Increasing The Tableware Glass Quality by Substituting CeO₂ In Place of Sb₂O₃

Abstract
Tableware glasses have extensively been used in daily lives. Not only functionality of tableware glass articles are significant but also aesthetic appearance take great importance. In this study, the increase in glass quality in terms of color aspects were worked. The goals are to improve glass quality, to increase aesthetically preferableness and to make cost effectiveness by adding cerium oxide in place of antimony trioxide in tableware glass articles of company. For that purpose, the addition of cerium oxide in pre-determined amounts was substituted for antimony trioxide to observe its effects on glass neutrality during real-time production activities had been continued in company. As a result of the study, with the addition of cerium oxide L* value was increased as 5.5%, the amount of zinc selenide and cobalt oxide decolorisation agents usage were decreased as 30% and 17%, respectively while 1% cost efficiency was achieved, and finally the purer, the sheeerer and neutral tableware articles were obtained.

Keywords
CeO₂; Glass; Sb₂O₃; Tableware.

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1. Introduction

Glass materials dating back to the Egyptian ancient times has come up with many improvements from past to present. From the first time of production to the days, the technology behind this development has been increasing day by day. Since high temperature conditions are dominant during glass production, determination of elevated temperature properties in glass melts takes great importance [1, 2]. Within the sort of glass materials, tableware glass production has a relatively significance that everyday glass articles have been produced by this class of materials. In the field of tableware glass production, the quality of glass in terms of designed shape consistency, targeted color view, zero glass defects, etc. are typically followed so as to achieve qualified glass articles.

Commercially, soda-lime-silica glass composition have been preferred in minor varying percentages of constituents with respect to companies’ way of competition strategies. Therefore, colors in soda-lime-silica glasses are targeted for commercial concerns. The color of glass articles are a consequence of coloring agents such as iron oxide, cobalt oxide, zinc selenide, etc. and can be performed as either intentionally or unintentionally [3]. In addition, redox state of glass melts have remarkable effect on resultant glass color. Since a great capacities like 150 or 250 or etc. tonnes per day have been produced in production facilities industrial grade raw materials have been preferred due to economical limitations. In here, industrial grade raw materials means reasonable iron oxide content of raw materials, i.e. ranging from 150 to 300 ppm, because the cost of raw material increases as purification process is carried out. For mentioned reasons, iron oxide content is inherently introduced into glass melts [4]. The redox equilibrium related to the iron in glasses occur, as given by Eq. (1):

\[ 4Fe^{2+} + O_2 = 4Fe^{3+} + 2O_2 \]  

(Eq. 1)

The multivalent character of iron in glass melt behaves as Fe$^{2+}$ to Fe$^{3+}$ under heating ambient and Fe$^{2+}$ causes blue-green hue whereas Fe$^{3+}$ yellow-green hue. Because blue-green hue is nearly tenfold forceful compared to yellow-green hue in terms of color obtained the reduction stage should be taken place in order to obtain qualified glass color [5]. In both cases, there occurs colorization effect of iron content. To eliminate the remaining color in glass article, color stabilizers or agents are added according to the remaining color hue. In general, industrial tableware glass producer companies prefer to use cobalt oxide for blue color resource and zinc selenide for pink color to neutralize glass color.

As a source of oxygen for reduction equilibrium equation stated in Eq. (1), antimony trioxide would rather preferred by most producers. According to the Eq. (2) and Eq. (3) given below:

\[ Sb_2O_3 + O_2 = Sb_2O_5 \]

\[ Sb_2O_5 = Sb_2O_3 + O_2 \]
Increasing The Tableware Glass Quality by Substituting CeO\textsubscript{2} In Place of Sb\textsubscript{2}O\textsubscript{3}.

Antimony trioxide takes reaction with oxygen in earlier temperature and the product of the Eq. (2) decomposes, ensuring oxygen to the system. The higher the amount of oxygen to the system the higher the reduction of iron content will. Therefore, cerium oxide becomes a candidate in place of antimony trioxide for that purpose due to the fact that the oxidizing power for a soda-lime-silica glass follows as Ce>Cu>Sn>As>Sb [6].

In this study, a glass company having 175 tonnes per day glass pull with end-port regenerative furnace combusted by natural gas was chosen. The ordinary soda-lime-silica production was carried out by using antimony trioxide for decolorisation purpose. Cerium oxide was substituted for antimony trioxide. The 35 days-trial regarding substitution will be given within below mentioned titles.

2. Experimental Procedure

2.1. Materials

Within the scope of this study, Soda-Lime-Silica made of silica sand, soda ash, dolomite, albite and calcite were used at a glass production company. Besides main starting raw materials, sodium sulphate, antimony trioxide and cerium oxide were introduced for glass quality improvement. Lastly, cobalt oxide and zinc selenide were added for neutral glass color obtainment.

2.2. Production

The company that glass samples produced has a commercial glass composition and only percentage intervals of each constituent was given due to confidential concerns. The glass composition and batches in terms of additives (Sb\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2}) were presented in Table 1. The experimental study were seperated into 2 steps: first Sb\textsubscript{2}O\textsubscript{3} was added in commercial glass composition with varying amounts without causing any quality problems in production lines due to the fact that ordinary glass production in company had been continued while experiment were performing, second CeO\textsubscript{2} was put in commercial glass composition with changing amounts same like Sb\textsubscript{2}O\textsubscript{3}.

Table 1: The prepared glass batches including codes, additives and amounts.

<table>
<thead>
<tr>
<th>Code No.</th>
<th>Additive Type</th>
<th>Amounts (\times 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A200</td>
<td>Sb\textsubscript{2}O\textsubscript{3}</td>
<td>1,65</td>
</tr>
<tr>
<td>A220</td>
<td>Sb\textsubscript{2}O\textsubscript{3}</td>
<td>1,80</td>
</tr>
<tr>
<td>A230</td>
<td>Sb\textsubscript{2}O\textsubscript{3}</td>
<td>1,95</td>
</tr>
<tr>
<td>A240</td>
<td>Sb\textsubscript{2}O\textsubscript{3}</td>
<td>2,10</td>
</tr>
<tr>
<td>S400</td>
<td>CeO\textsubscript{2}</td>
<td>3,30</td>
</tr>
<tr>
<td>S450</td>
<td>CeO\textsubscript{2}</td>
<td>3,75</td>
</tr>
<tr>
<td>S500</td>
<td>CeO\textsubscript{2}</td>
<td>4,15</td>
</tr>
<tr>
<td>S800</td>
<td>CeO\textsubscript{2}</td>
<td>6,75</td>
</tr>
</tbody>
</table>

After different batches were determined, starting raw materials were scaled, mixed and transferred to the glass melting furnace. The melting furnace has 175 tonnes per day production capacity, and natural gas combustion takes place in end-port design with regenerative gas chamber. In Fig.1, the detail drawing of glass melting furnace was revealed. The batches were introduced from #6 to # 5. The melted glass goes through #7 for conditioning, and refined glass melt transfers to #8-14 for equalizing before forming step. The gases occured as a result of melting are discharged throughout #4 to 1.
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Fig. 1: The layout of glass melting furnace (1: chimney, 2: flue line channel, 3: regenerators, 4: ports, 5: melting area, 6: batch introduction, 7: distributor, 8-14: forehearts).

The melting temperature was recorded as 1455 °C for both different additives, and annealing was carried out at 560 °C for 1h. The glass composition interval was listed in Table 2. The reason behind presenting content intervals was about commercial confidentiality.

Table 2: Glass composition intervals for each constituent.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>% wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>70,50-72,00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1,40-1,70</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0,02-0,03</td>
</tr>
<tr>
<td>CaO</td>
<td>7,80-8,40</td>
</tr>
<tr>
<td>MgO</td>
<td>3,40-3,90</td>
</tr>
<tr>
<td>Na₂O</td>
<td>13,90-14,50</td>
</tr>
<tr>
<td>K₂O</td>
<td>&lt;0,33</td>
</tr>
<tr>
<td>TiO₂</td>
<td>&lt;0,11</td>
</tr>
<tr>
<td>SO₃</td>
<td>0,15-0,30</td>
</tr>
</tbody>
</table>

The production duration for experimental studies took 35 days in total due to the fact that observing the resultant effect of each varying amounts of additives took 4 days.

2.3. Characterisation

Following glass samples production, chemical composition of samples was determined via XRF (Bruker S4 Pioneer, England). The structural properties were measured via XRD (Rigaku Rint 2000, Turkey) while the optical properties were figured out via UV/Vis spectro-photometer (Perkin Elmer Lambda 650S, Turkey). And lastly, the reduction of Fe²⁺ to Fe³⁺ ratio was calculated by using UV/Vis/NIR (Shimadzu 3600, England) and XRF (Bruker S4 Pioneer, England). In addition, glass densities were measured by using Archimedes’ principles (Turkey).

3. Results & Discussion

The images of glass articles produced were revealed in Fig.2 highlighting that cups and jars having two different additives under UV light, respectively. In both figures, left hand side articles represents Sb₂O₃ added glass samples whereas right hand side articles for CeO₂ ones. Both images
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indicate that cerium oxide added glass articles have higher brightness in comparison to antimony oxide added under UV light ambient.

The minerological measurements via XRD analysis were presented in Fig. 3. Both analyses showed the amorphous structure of glass materials irrespective of varying additive amounts. It was also determined that there was no other crystalline phases. In addition, as antimony trioxide amount increased the humped peak became narrower between 19-45° degrees. On the other hand, cerium oxide showed narrower humped peaks compared to antimony oxide ones.

Fig. 2: Images of glass articles produced (left: cups; right: jars)

The color of glass articles were highlighted via UV/Vis measurements by preferring L’a’b’ coordinate system. All samples were randomly selected from production lines for each of trials during 35 days. The color analysis in terms of a’ and b’ was shown in Fig. 4. Besides, the color space was illustrated in Fig. 5 to ensure better understanding in color perspective. In Fig. 4, the glass color was placed through green-blue region, particularly near to green side in the beginning (1th & 7th days), however it moved throughout red-yellow region, particularly pinkish (28th & 35th days), at the end as substituting cerium oxide in place of antimony trioxide.

Fig. 3: X-ray diffraction measurements of glass articles produced. (Left: Sb$_2$O$_3$ added glass articles from up to down A200, A220, A230, A240; Right CeO$_2$ added glass articles from up to down S400, S450, S500, S800).

Fig. 4: Images of glass articles produced (left: Sb$_2$O$_3$ added glasses; right: CeO$_2$ added glasses).
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Along with the trial days, the pigments stabilizing glass color, cobalt oxide and zinc selenide, were adjusted with respect to color analysis because the company continued to real time production routes.

**Fig. 4:** Color measurements of glass articles produced in terms of a’ & b’.

**Fig.5 :** The color space.
The amounts of color stabilizers of cobalt oxide and zinc selenide during trial days were presented in Fig. 6 and Fig. 7, respectively. As indicated in figures that both stabilizer agents were in a decreasing trend as cerium oxide was introduced into the glass system. That is, zinc selenide usage was decreased from \(3.60 \times 10^{-3}\) to \(2.50 \times 10^{-3}\) wt.% whereas cobalt oxide was diminished from \(2.30 \times 10^{-4}\) to \(2.00 \times 10^{-4}\) wt%.

In addition to \(a'\) and \(b'\) values, brightness, \(L^*\), values of glass systems in terms of antimony trioxide and cerium oxide was given in Fig. 8. In the beginning of trial days, namely antimony trioxide usage, the \(L^*\) value was about 90 over 100, however as cerium oxide had been started to be introduced into the glass system, \(L^*\) value was gradually increased, reaching up to nearly 95, at the end of the trial. As seen that there occured some fluctuations along with the trial days, this could be considered as neglected.

The result of iron oxide to total iron ratio was presented in Table 3. Two different additive amounts for each of additive types were clearly listed. It can be seen that total iron amount was constant for each glass which supports that raw materials were kept constant in quality. As cerium oxide and antimony trioxide additives were added into glass with increasing amount the amount of iron (III) oxide to iron (II) oxide ratio increased, meaning that the reduction of iron was achieved in a good way. However, cerium oxide has a double effect on this ratio, namely 8.153 at its highest addition whereas 4.122 for antimony trioxide at its highest addition. Therefore, it can be stated that cerium oxide has better effect on glass quality rather than antimony trioxide.
Table 3: Iron oxide rations of glass articles produced.

<table>
<thead>
<tr>
<th></th>
<th>Sb₂O₃ doped</th>
<th>CeO₂ doped</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A200</td>
<td>A240</td>
</tr>
<tr>
<td>Fe³⁺ / Fe²⁺ Ratio</td>
<td>3,884</td>
<td>4,122</td>
</tr>
<tr>
<td>Fe²⁺ / Total Fe Ratio</td>
<td>0,205</td>
<td>0,187</td>
</tr>
<tr>
<td>Total Fe</td>
<td>0,025</td>
<td>0,025</td>
</tr>
</tbody>
</table>

4. Conclusions
The conclusions of the present study can be listed as follows:

- The glass composition of the study is mainly composed of Na₂O+K₂O as 15%, CaO+MgO as 13%, Al₂O₃ as 2% and Fe₂O₃ as 0,025%.
- The images under UV light show that cerium oxide has a higher effect on brightness in comparison to antimony trioxide.
- The glass articles having different shape as cup and jar present higher brightness by using cerium oxide.
- The hump occurred between 19-45° moves towards to lower degrees as antimony trioxide amount increases in x-ray diffraction analysis. Indeed, the hump of diffraction analysis is wide with lower additive amounts while narrower humps occur as additive amounts increase. It is found out that the diffraction patterns of cerium oxide show narrower peaks compared to antimony trioxide.
- It is ascertained that the color of glass article moves from green-yellow nearing to yellow region as cerium oxide amount is increased in glass system.
- The L* value of glass articles are sharply increased from 90 to 95 over 100 with the increment of cerium oxide in place of antimony trioxide. It is stated that cerium oxide have a positive effects on both color and brightness.
- The color stabilizers of cobalt oxide and zinc selenide amounts are dramatically decreased as cerium oxide is introduced into glass system with increasing amounts. It is determined that optimum addition amounts are about 0,00020% and 0,0025% for cobalt oxide and zinc selenide, respectively under the circumstances of iron oxide amount as 0,025%.
- The usage of color stabilizers are decreased as 17% and 29% for cobalt oxide and zinc selenide, respectively.
- The reduction of iron (II) oxide to iron (III) oxide percentage are increased with the addition of cerium oxide as double in comparison to antimony trioxide. As a consequence of reduction percentage increment, the adverse effects of iron (II) oxide on color is diminished.

5. References
[1]: J. E. Shelby, Int. to Glass Sci. and Tech. 2nd Edi., 2005, pp. 4-5.
[3]: Aydin E., (2015), Cam Üretiminde Sorunlu
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