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Sb_2O_3 Yerine CeO_2 Kullanımı İle Sofra Camı Eşyalarında Kalitenin Arttırılması

Recep KURTULUŞ[1], Veli UZ[2]

[1] *Afyon Kocatepe University, Department of Materials Science and Engineering, Afyonkarahisar.*

[2] *Kütahya Dumlupınar University, Department of Metallurgy and Materials Engineering, 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

Günlük hayatımızda sofra camı eşyaları bir hayli kullanım görmektedir. Sofra camı eşyalarının sadece işlevselliği önemli olmamakta, aynı zamanda estetik açıdan görünümleri de önem taşımaktadır. Bu çalışmada, renk görünümüne bağlı olarak kalitede artış sağlanması çalışılmıştır. Üretim tesisinde halihazırda üretilmekte olan sofra camı eşyalarında antimuan trioksit yerine seryum oksit katılması ile cam kalitesinin iyileştirilmesi, estetik seçilebilirliğin arttırılması ve maliyetin düşürülmesi hedeflenmiştir. Bu amaçla, üretim aktiviteleri boyunca kesinti vermeksizin önceden belirlenen seryum oksit miktarlarının katkılandırılması ile cam nötralitesi üzerindeki etkileri gözlemlenmiştir. Sonuç olarak, antimuan trioksit yerine seryum oksit kullanımı sayesinde camın parlaklığı, L*, % 5,5 arttırılmış, çinko selenit ve kobalt oksit kullanımları sırasıyla %30 ve % 17 azaltılmış ve nihayetinde daha saf ve daha parlak nötral sofra camı eldesi sağlanmıştır.

Anahtar kelimeler

Cam; CeO_2; Sb_2O_3; Sofra Eşyası.

Increasing The Tableware Glass Quality by Substituting CeO_2 In Place of Sb_2O_3

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 sheerer and neutral tableware articles were obtained.

Keywords

CeO_2; Glass; Sb_2O_3; 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 thesedays, 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 comptetition 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 intentially or unintentially [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 :

$Sb_2O_3 + O_2 = Sb_2O_5$

$Sb_2O_5 = Sb_2O_3 + O_2$

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 substittution 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_2O_3 and CeO_2) were presented in Table 1. The experimental study were seperated into 2 steps : first Sb_2O_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_2 was put in commercial glass composition with changing amounts same like Sb_2O_3.

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

Code No.	Additive Type	Amounts (/10^5)
A200	Sb_2O_3	1,65
A220		1,80
A230		1,95
A240		2,10
S400	CeO_2	3,30
S450		3,75
S500		4,15
S800		6,75

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.

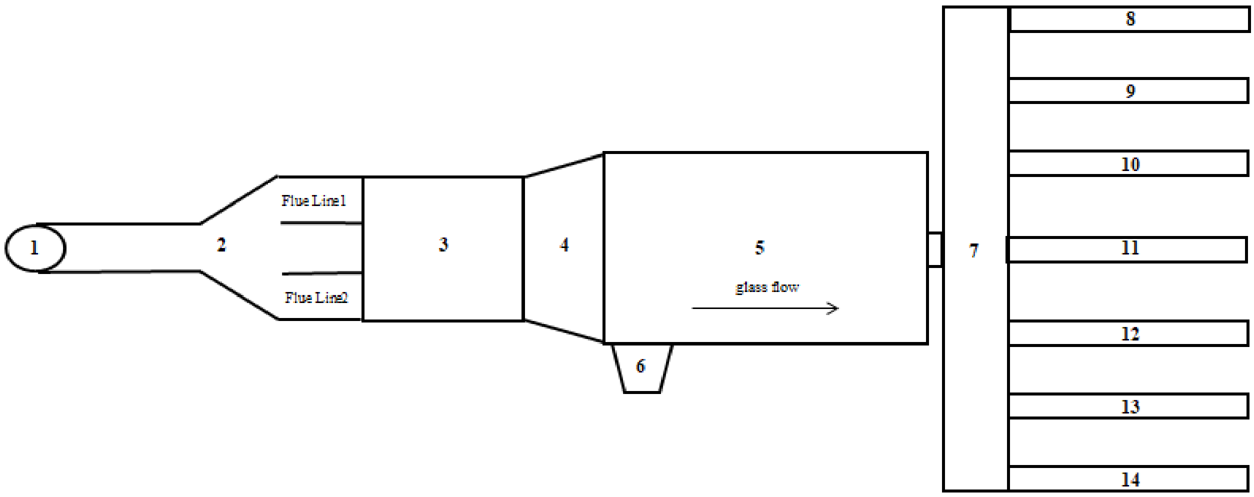

Fig. 1: The layout of glass melting furnace (1: chimney, 2: flue line channel, 3: regenerators, 4: ports, 5: melting area, 6: batch introduction, 7: distributor, 8-14: forehearths).

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 behing presenting content intervals was about commercial confidentiality.

Table 2: Glass composition intervals for each constituent.

Constituent	% wt.
SiO_2	70,50-72,00
Al_2O_3	1,40-1,70
Fe_2O_3	0,02-0,03
CaO	7,80-8,40
MgO	3,40-3,90
Na_2O	13,90-14,50
K_2O	<0,33
TiO_2	<0,11
SO_3	0,15-0,30

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 Fe^{2+} to Fe^{3+} ratio was calculated by using UV/Vis/NIR (Shimadzu 3600, England) and XRF (Bruker S4 Pioneer, England). In additon, 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 Sb_2O_3 added glass samples whereas right hand side articles for CeO_2 ones. Both images indicate that cerium oxide added glass articles have higher brightness in comparison to antimony oxide added under UV light ambient.

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

The minerological measurements via XRD analysis were presented in Fig. 3. Both anaylsis 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.

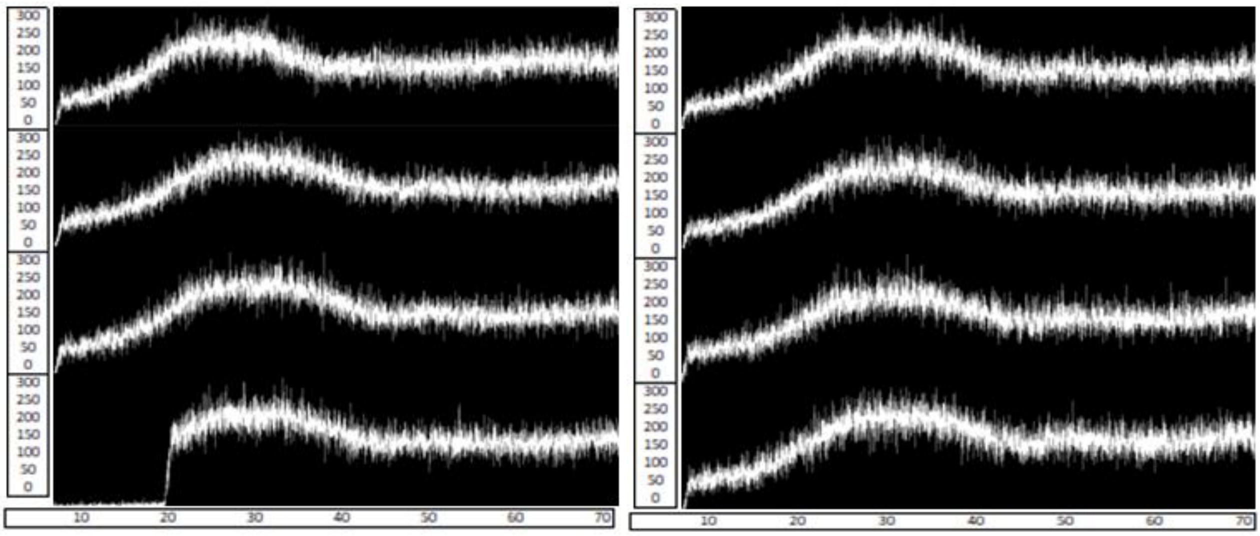

Fig.3: X-ray diffraction measurements of glass articles produced. (Left: Sb_2O_3 added glass articles from up to down A200, A220, A230, A240; Right CeO_2 added glass articles from up to down S400, S450, S500, S800).

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.

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.

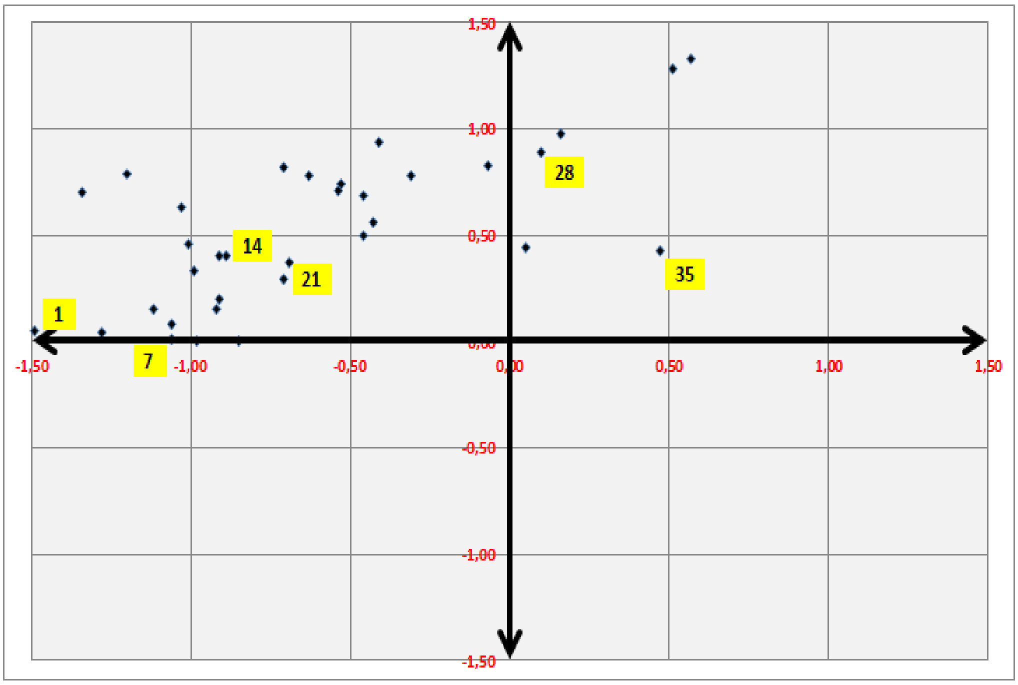

Fig. 4: Color measurements of glass articles produced in terms of a' & b'.

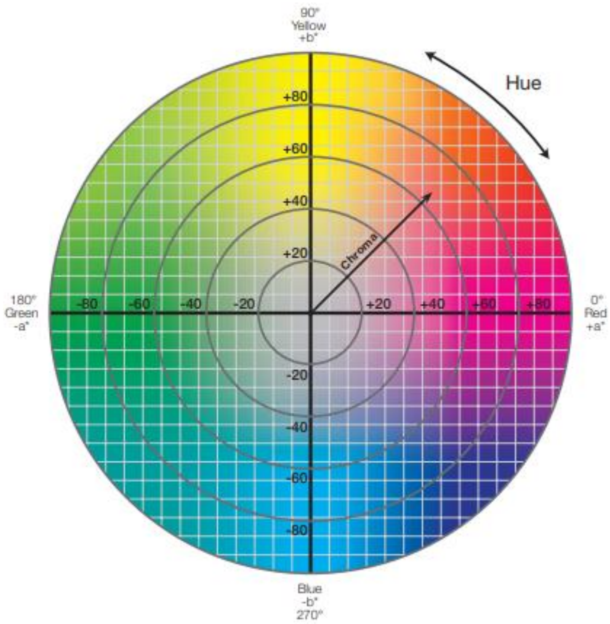

Fig.5 : The color space.

The amounts of color stabilizers of cobalt oxide and zinc selendie 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 $3{,}60\times10^{-3}$ to $2{,}50\times10^{-3}$ wt.% whereas cobalt oxide was diminished from $2{,}30\times10^{-4}$ to $2{,}00\times10^{-4}$ wt%.

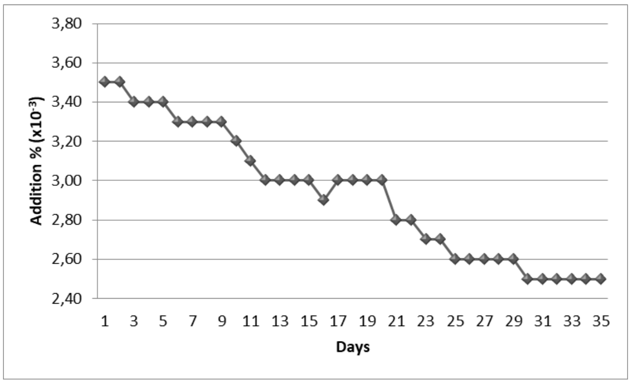

Fig. 6: The usage of zinc selenide (wt.%) during trial days.

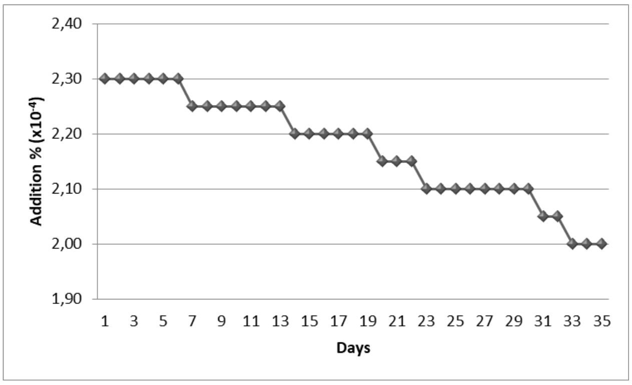

Fig. 7: The usage of cobalt oxide (wt.%) during trial days.

In addition to a’ and b’ values, brightness, L*, values of glass systems in terms of antimony trioxe and cerium oxide was given in Fig. 8. In the beginnnig 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.

Fig. 8: Brightness, L*, values of glass systems in terms of antimony trioxe and cerium oxide during 35 days.

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.

	Sb_2O_3 doped		CeO_2 doped	
	A200	A240	S400	S800
Fe^{3+} / Fe^{2+} Ratio	3,884	4,122	7,950	8,153
Fe^{2+} / Total Fe Ratio	0,205	0,187	0,125	0,109
Total Fe	0,025	0,025	0,025	0,025

4. Conclusions

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

- The glass composition of the study is mainly composed of Na_2O+K_2O as 15%, CaO+MgO as 13%, Al_2O_3 as 2% and Fe_2O_3 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 green region to yellow-red 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 circumtances 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.

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