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EXPERIMENT IN RECOLORING GLASS MELT MADE WITH SLAG BATCH

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The regimes for recoloring glass melt in the commercial furnaces at the Chagodoshchenskii Glass Works and K JSC, which operate with slag batches, are analyzed. It is shown that the efficiency of the process of changing the color of the glass is determined by, first and foremost, the rational regime for changing the composition and redox potential of the batch.

Key words: glass containers, color, batch, slag, redox potential, process monitoring.

Glass containers are widely used for packaging food, chemical, perfume, cosmetic, and pharmaceutical products because of their obvious and unquestionable competitive advantages:

– permit avoiding adverse effects of sunlight on the contents, which keeps the product from spoiling and increases its shelf-life;

– do not interact with its contents, thereby assuring a high degree of hygiene;

– are completely impermeable to gases, making it possible to create hermetic packaging;

– permit bottling beverages under pressure (champagne and sparkling wines);

– demonstrate diversity of shapes and designs, which secures product recognition, prevents counterfeiting of products, and increases sales volume.

High quality products are well preserved in hygienic and safe glass containers; they remain fresh and retain their natural flavor. “Anyone who wants to be healthy trusts glass” is the opinion of 88% of European consumers [1].

One index for regulating the quality of glass containers is the color of the glass, which determines mainly the protective functions of the packaging [2]. According to GOST R 52022–2003 “Glass containers for food and perfume and cosmetics products: Types of glass” the following types of containers are produced: colorless — BT-1 and BT-2; half-white — PT; green — ZT-1 and ZT-2; and, brown — KT. In addition, glass with other hues can be obtained on the basis of green and brown glass: emerald-green — ZTi, yellowish-green — ZTzh, brownish-green — ZTk; dark-brown — KTt, and yellowish-brown — KTzh.

The competition, which increases every year, in the production of glass containers as well as the requirements of foreign companies using glass containers have led to an approach to evaluating glass color and hue that is more stringent and detailed than in GOST 52022–2003. These requirements include monitoring the light transmission in the visible and ultraviolet parts of the spectrum, the degree of saturation of the color, the dominant wavelength, the color coordinates, and other optical characteristics [3].

Russian producers of glass containers who in recent years have been working in a very competitive environment use different methods in an attempt to reduce expenses and occupy available niches in the glass market. A change in the color of glass containers is one of the methods used to meet the demand and keep their share of the market. The glass melt is recolored in brown or green at enterprises in a continuous glass-making regime in a glassmaking furnace. It should be noted that this method is economically efficient only in the production of large batches of glass containers of the same color.

Changing the color of glass melt in a high-capacity furnace (of the order of 300 – 400 tons/day) could take about one week and as a rule entails high energy consumption and losses of glass melt. Nonetheless, enterprises must take this step for a number of reasons. The modern market for glass

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TABLE 1. Recommended ORP of Batches for Container Glass [6]

Glass type	ORP
Green	+20
Colorless, oxidized	+5 ... +20
Colorless, reduced	+1 ... +5
Green emerald	+1 ... –10
Amber	–25 ... –30

containers dictates quite frequent transitions from one glass color to another.

Chagodoshchenskii Glass Works and K, JSC, produces colorless, green, olive, and brown glass containers. A particularity of the production of glass containers is the use of blast furnace slag, obtained from the metallurgical combine Severstal’, as the main raw material, whose green glass content reaches 15% and the brown glass content 20% or more [4].

Three technological operations for changing the color of the glass melt in commercial furnaces without stopping production (in the on-line regime) were conducted at the enterprise in the last two years:

1) coloring colorless glass melt in green in a 190 tons/day furnace;

2) recoloring the glass melt from green to brown in two furnaces with capacity 190 and 275 tons/day.

Changing the color of the glass melt entailed changes in the temperature and gas regimes of the furnace and production channels, the dynamics of the convective motion of the glass melt, the feed regime, and other process parameters. However, the redox potential (ORP) of the batch (Table 1), which determines the state of the polyvalent elements in the composition of the glass (sulfur, iron, carbon), was the determining factor for the transition from one color of the glass melt to another [5, 6].

The first process operation, associated with very small changes in the composition of the glass and the batch recipe, was completed most easily and simply (Table 2).

The process of coloring the glass melt required 40 h after the loading of the green batch (Table 3), which contained slag — a reducing material with up to 0.85% (by weight) of sulfide sulfur, was started.

It should be noted that the weight content of sodium sulfate (referred to simply as sulfate in what follows) in the green batch was increased gradually in order to avoid strong foaming up of the glass melt as a result of intense interaction between the sulfate and sulfide sulfurs:

$$S^{2-} + 3SO_4^{2-} \leftrightarrow 4SO_2 + 4O^{2-};$$

$$3S^{2-} + SO_4^{2-} \leftrightarrow 2S_2 + 4O^{2-}.$$

This gave the required redox potential (ORP). In addition, the ORP of the batch varied in the course of the experiment from –13.9 units (reductive) for the first-load batches to +2.7 units (oxidative) for the final composition of the batch. The foaming of the glass melt was observed during the first 5 – 7 h from the start of the experiment.

The glass melt acquired a green color in 5 h in the doghouse area and in 10 h in the feeder channel. A stable saturated green color was established 1 day after the start of coloring in the doghouse area of the furnace and in 35 h in the feeder channel. The standardized indices are the color saturation 27 – 30% and the total light transmission 69 – 71%. The glass color was identified as emerald green.

A supposition arose during the analysis of the technological experiment that for green glass the required amount of sulfate (0.7% Na_2O introduced in the sulfate form) should be added directly into the batch. In addition, its ORP will be close to the value for colorless glass melt, and strong foaming should not be observed in the doghouse or in the melting

TABLE 2. Change in the Composition of the Glass and Batch Recipe in the Process of Coloring Colorless Glass Melt in Green Color

Oxides	Oxide content, wt.%, in glass		Batch		
			Material	Weight content of material per 100 glass parts	
	colorless	green		colorless	green
SiO_2	72.65	70.85	Sand	65.96	65.46
Al_2O_3	2.00	1.75	PShK [Feldspar-quartz]	10.57	–
Fe_2O_3	0.05	0.70	Slag	–	13.70
Cr_2O_3	–	0.70	Chalk	22.73	–
CaO+MgO	12.20	12.60	Dolomite	–	10.93
Na_2O^*	13.10	13.40	Soda	20.54	22.13
* Note	0.20% Na_2O introduced as sulfate	0.70% Na_2O introduced as sulfate	Sulfate	0.49	1.63
			Portachrom	–	1.84
			Pigment Fe	–	0.29
			ORP	+10.0	+2.7

TABLE 3. Monitoring the Process of Green Coloring of Colorless Glass Melt

Coloring process time, h	Batch		Color of glass melt samples	
	Recipe change	ORP	in doghouse area	in channel
0	Introduced into green batch. Batch : cullet = 50 : 50; 0.35% Na_2O (sulfate)	–13.9	Colorless	Colorless
5	Foaming is observed. 0.35% Na_2O (sulfate)	–13.9	Appearance of glass hue	Colorless
10	0.45% Na_2O (sulfate)	–9.2	Green	Appearance of glass hue
16	0.45% Na_2O (sulfate)	–9.2	Green: S^* = 10%; T^{**} = 78.3%	Green
24	0.65% Na_2O (sulfate)	+0.3	Green: S^* = 18%; T^{**} = 73.8%	Green
31	Batch : cullet = 60 : 40; 0.65% Na_2O (sulfate)	+0.3	Green: S^* = 23%; T^{**} = 73.1%	Green
35	0.70% Na_2O (sulfate)	+2.7	Green: S^* = 27%; T^{**} = 70.9%	Green: S^* = 27%; T^{**} = 70.9%
40	0.70% Na_2O (sulfate)	+2.7	Green: S^* = 29%; T^{**} = 69.6%	Green: S^* = 29%; T^{**} = 69.6%

* Color saturation.

** Color transmission.

zone of the furnace. However, these suppositions must be tested and checked under production conditions.

In the recoloring variant 2 the ORP of the batch changed significantly: from oxidative +10.3 for green glass to reductive –23 for brown glass (Table 4). In addition, it takes more time and is more complex.

At the same time, with the exception of the removal of the colorant Cr_2O_3, the basic composition of the glass hardly changed. The changes in the batch were made for the purpose of creating a reducing potential by decreasing the fraction of sodium sulfate and introducing coal in amounts to 17 wt.% sulfate as well as increasing the amount of slag by a small amount (see Table 4).

The recoloring process lasted for 5 days, during which the content of the main raw materials was adjusted, portachrome was removed from the batch, the amount of sulfate was adjusted, and carbon was introduced into the batch. All actions were performed in steps keeping the glass melt level unchanged and not permitting significant foaming or the appearance of seeds in the bottle glass (Table 5).

The working reductive potential of the batch reached its maximum values (from –30 to –32 units) in one day and was kept at this level for the next 2 days, after which it was lowered to the standard values (–23) (see Table 5). This dynamics of the change in the ORP of the batch made it possible to consistently attain a reductive potential by mixing glass melts of different types and to form coloring structural groups of the amber chromophore $[Fe^{3+}O_3S^{2-}]^{5-}$.

The glass took on a brown color as a result of the presence of chromophoric groupings, each of which consists of a central ion Fe^{3+} in tetrahedral coordination, three oxygen ions, and one ion S^{2-}. The excess negative charge of a grouping is neutralized by sodium ions Na^+. The spectral light transmission curves of such glasses are characterized by

TABLE 4. Change in the Composition of Glass and Batch Recipe in the Process of Recoloring Glass Melt from Green to Brown

Oxides	Oxide content, wt.%, in glass		Batch		
	green	brown	Material	Weight content of material per 100 glass parts: green	brown
SiO_2	71.56	71.82	Sand	70.3	70.13
Al_2O_3	1.75	1.80	Slag	7.03	8.46
Fe_2O_3	0.43	0.38	Dolomite	17.01	15.82
Cr_2O_3	0.26	–	Soda	21.93	22.35
CaO + MgO	12.60	12.60	Sulfate	1.31	0.70
Na_2O^*	13.40	13.40	Portachrom	0.62	–
* Note	0.56% Na_2O introduced as sulfate	0.30% Na_2O introduced as sulfate	Pigment Fe	0.03	0.16
			Carbon	–	0.12
			ORP	+10.3	–23.0

TABLE 5. Monitoring of the Recoloring of Glass Melt from Green to Brown

Day No.	Time, h:min	Changes in batch recipe	ORP	Color of glass sample		Notes
				in doghouse area	in channel	
1	8:00	Increase of slag in batch. 0.10% Na_2O (sulfate), 10% carbon*	–17.6	Green	Green	Bottles packed as grade 1
	14:00	0.15% Na_2O (sulfate), 30% carbon*	–24.9	Light green	Green	Bottles packed as grade 2
	21:00	0.20% Na_2O (sulfate), 30% carbon*	–27.4	Light green	Light green	One automatic glass forming machine SFA retained
2	8:00	0.20% Na_2O (sulfate), 35% carbon*	–30.4	Light olive	Light olive	No output for sale
	16:00	0.30% Na_2O (sulfate), 35% carbon*	–32.6	Dark olive	Light olive	
3	9:30	0.30% Na_2O (sulfate), 30% carbon*	–32.3	Light brown	Light brown	
4	9:00	0.30% Na_2O (sulfate), 25% carbon*	–27.6	Brown	Brown	Packing of Baltika bottles started
	18:00	0.30% Na_2O (sulfate), 20% carbon*	–23.0	Brown	Brown	Packing of Ayan bottles started
5	16:00	0.30% Na_2O (sulfate), 20% carbon*, 10% brown recycled cullet	–23.0	Brown	Brown	Packing of brown bottles

* Carbon was introduced from sulfate mass.

TABLE 6. Change in the Color Characteristics of Glass in the Recoloring Process

Day	Transmission *T*, %	DWL, nm	Brightness *B*, %	Saturation *S*, %
1	73.33	546.3	37.15	16.0
2	70.75	554.5	40.02	25.5
3	39.41	576.2	48.69	87.0
4	33.18	579.5	47.83	92.0
5	43.06	578.4	47.54	88.0

practically total absorption in the UV, violet, and blue ranges, which imparts different protective properties to the glass containers.

The standard color characteristics of the glass were attained quite quickly (Table 6). In addition, there were only two days on which products for sale were not produced.

Industrial experiments showed that glass melt made from slag batch can be recolored in a continuous regime in high-capacity industrial furnaces. The technological recoloring process is a multifactor process, and as a result it can be implemented in alternative regimes, including the most efficient ones under concrete conditions.

One of the most significant factors of the process of recoloring glass melt is the magnitude and dynamics of the ORP of the batch. Since the stability of the glass melting process and the efficiency of fining of the glass melt also depend on this parameter, it was proposed that the ORP of the batch be constantly monitored by computational and analytical methods.

The dynamics of the sodium sulfate introduced should be approached in a well-grounded manner. As a rule, when this component is present in excessive amounts, bubbles and seeds form in the glass melt when too much of this component is present and the fining process is impeded when there is too little.

The date of the recoloring of the glass melt should be known beforehand so that this technological process can be conducted in a well-grounded manner; all technological operations can be conducted gradually in accordance with the technological regime worked out.

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