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Sanat&Tasarım Dergisi,14(2),2024:131-146
Araştırma Makalesi / Research Article
Geliş Tarihi / Received: 06.01.2024
Kabul Tarihi / Accepted: 07.05.2024
DOI: 10.20488/sanattasarim.1602393

INVESTIGATING DECORATIVE EFFECTS OF METAL SALTS IN HOT GLASS FORMING METHODS

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ABSTRACT

Glass is a material of great significance, especially for artistic expressions, due to its aesthetic and decorative qualities. Glass decoration holds a prominent place in aesthetics and possesses an ever-evolving nature. For centuries, decorative effects have been created on the surface of glass using various methods and techniques, and since the times of Ancient Egypt and Rome, the widespread adoption of this practice has led to the attainment of unique colors and textures. Today, thanks to advancements in technology, glass decoration continues to evolve with new ideas and techniques. These developments continue to serve as a major source of inspiration for artists. Artists develop different decoration techniques during workshop sessions as their interest in experimental approaches increases, thereby contributing to the aesthetic structure of glass. This study aims to investigate the effects of using different water-soluble metal salts in hot glass shaping methods on surface decoration in glass art, with the goal of offering new and original possibilities. The research seeks to contribute to the exploration of alternative designs on hot glass surfaces by glass artists, allowing them to create unique forms and gain new avenues of expression by utilizing the various effects of metal salts. 4 water-soluble metal salts were selected for use in experimental studies. Artistic effects on glass surfaces were supported by experimental work. The metal salts were applied to the glass surface using the fusion technique, and the resulting pieces were combined through the hot glass shaping technique. In this context, the aim is to present a study that will serve as an example of the potential applications of the combined use of hot glass blowing technique and fusion technique.

Keywords: *Glass art, Surface decoration, Water-soluble metal salts, Design.*

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SICAK CAM ŞEKİLLENDİRME YÖNTEMLERİNDE METAL TUZLARININ DEKOR ETKİLERİNİN İNCELENMESİ

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ÖZET

Cam, estetik ve dekoratif nitelikleri nedeniyle özellikle sanatsal ifadeler için büyük öneme sahip bir malzemedir. Yüzyıllardır çeşitli yöntemler ve teknikler kullanılarak camın yüzeyinde dekoratif etkiler oluşturulmuş ve Antik Mısır ve Roma dönemlerinden itibaren bu uygulamanın yaygınlaşmasıyla özgün renkler ve dokular elde edilmiştir. Bugün, teknolojideki ilerlemeler sayesinde cam dekorasyonu, yeni fikirler ve tekniklerle evrimini sürdürmektedir. Bu gelişmeler, sanatçılara büyük ilham kaynakları sunmaktadır. Sanatçılar, atölye çalışmaları sırasında deneysel yaklaşımlara olan ilgilerinin artmasıyla farklı dekorasyon teknikleri geliştirirler ve böylece camın estetik yapısına katkı sağlarlar. Bu çalışma, sıcak cam şekillendirme yöntemlerinde suda çözünen farklı metal tuzlarının kullanımının cam sanatında yüzey dekorasyonu üzerindeki etkilerini araştırarak, yeni ve özgün olanaklar sunmayı hedeflemektedir. Bu araştırma, cam sanatçılarının sıcak cam yüzeylerinde alternatif tasarım arayışlarına katkı sağlama amacı gütmekte olup, metal tuzlarının sunduğu çeşitli etkileri kullanarak benzersiz formlar oluşturmayı ve yeni ifade olanakları elde etmeyi amaçlamaktadır. Deneysel çalışmalarda kullanılmak üzere 4 adet suda çözünen metal tuzu seçilmiştir. Cam yüzeyleri üzerindeki artistik etkiler, deneysel çalışmalar ile desteklenmiştir. Metal tuzları cam yüzeyine füzyon tekniği kullanılarak uygulanmış ve elde edilen parçalar sıcak cam şekillendirme tekniği ile birleştirilerek özgün tasarımlar üretilmiştir. Bu bağlamda sıcak cam üfleme tekniği ve füzyon tekniğinin bir arada kullanım olanaklarına da örnek oluşturacak bir çalışma sunmak amaçlanmıştır.

Anahtar Kelimeler: *Cam sanatı, Yüzey dekorasyonu, Suda çözünen metal tuzları, Tasarım.*

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1. INTRODUCTION

Within craft traditions, glass presents a particularly fruitful area for the examination of artistic strategies that embrace and can be defined as adaptive, in relation to the interplay between the old and the new (Chambers and Oldknow, 2019). A few centuries ago, working on glass often meant adding tints to the texture of the medium to create a variety of textures, and then heat treating or 'firing' these onto the surface. Back then, glass craftsmanship wasn't actually an art; rather, it was a functional craft expressing visual appeal. Artistic glass, besides its aesthetic appeal, holds historical and cultural significance. Throughout history, glass has been used to create decorative and functional objects symbolizing wealth, craftsmanship, and cultural heritage. Contemporary glass artists blend historical influences with a quest to push creative boundaries in the medium (http 1).

Glass, encountered in many aspects of our lives, has maintained its popularity for centuries due to its versatile uses. Typically chosen in transparent or opaque forms, glass is an inorganic solid material that, when cooled, becomes brittle and hard, and when heated, transforms into a fluid allowing containment of liquids (Ağatekin, 2023; Özkaya, 2019).

The transparency of glass is a significant feature that allows for numerous unique and enchanting creative possibilities in the art world. When the possibilities of shaping glass limitlessly come together with the effects of color and light, it enables us to achieve unique artistic effects using glass as an art material. On the other hand, the variability of glass texture is the biggest feature that makes glass different from other materials. Materials like wood, metal, fibers, etc., tend to be relatively stable in terms of texture. In contrast, the texture of glass allows for the attainment of desired effects based on the raw material composition and applied techniques. Different chemical compounds and elements in the glass can have different effects on the color formulation. Even slight changes in material composition will produce different color effects, offering more opportunities and space for creation in glass art (He, 2016).

Glass, which is both an aesthetic and decorative material, is an important option especially for artistic expressions. Glass artists, designers and manufacturing factories use various decoration techniques during the production phase or on the final product to increase and improve the aesthetic value of the works. The methods used in the decoration of glass vary among themselves (Özkaya, 2019).

There are a wide variety of decoration techniques in glass art. These techniques allow us to highlight the exciting, infinitely variable nature of glass. Etching, sandblasting, cutting, engraving, painting and screen printing etc. are the main glass decoration techniques (Rich, 1988; Hemp, 1995). These techniques transform glass into a material that is more communicative, visually stunning, and instantly designable.

In the disciplines of art and design, the development of innovative and aesthetically rich artistic glasses with remarkable optical and structural properties that encourage creativity and facilitate the development of new forms and products represents an important field of academic research today. In this context, the exploration of new materials, methods, and techniques aims to contribute to the evolution and enhancement of the potential of glass art. Collaborations between materials science, chemistry, physics, and related disciplines in efforts to enhance the optical properties of glass, such as controlling light and manipulating colors and textures, will lead to the emergence of innovative solutions and innovative ideas. In this context, this study investigates the effects of water-soluble metal salts in hot glass shaping techniques on the surface decoration of artistic glass to enrich color and texture effects. It is aimed to contribute to glass artists' search for alternative surfaces on hot glass surfaces and to enable them to create original forms and obtain new expression opportunities with the different effects of metal salts. Four water-soluble metal salts were selected to be used in experimental studies. Mainly fusion and hot glass blowing techniques were used with a patchwork approach in hot glass production.

1.1. Water Soluble Metal Salts

Metal salts are compounds that can dissolve in water and ionize. These salts typically contain metal cations and non-metal anions.

Water-soluble metal salts are simple solutions consisting of nitrate, chloride and sulfate forms dissolved in water. Nitrates, chlorates and acetates of all metals and chlorides, bromides and iodides of all metals except lead, silver and mercury are soluble in water (Turner, 2009; Berthouex and Brown, 2017).

The test tube experiment can be used as an effective and simple method to quickly and visually determine the water solubility of a solid. The test is performed on 1 gram of solid sample added to approximately ½ inch of water. The tube is shaken to observe whether the sample dissolves. If dissolution is occurring, symptoms such as a change in the color of the water, softening of the solid particles, or a decrease in the volume of the solid may be observed. If there are no observations, the sample is either insoluble or only slightly soluble (Houghton, 2009).

As ionic substances most alkali metal salts and many alkaline earth metals salts dissolve in water (Ghosh and Berg, 2014).

Rules for estimating the solubility of an inorganic compound are presented in Table 1 (Russell, 2019).

Table 1. *Solubility rules for simple inorganic compounds in water.*

Rule Number	Rule
1	Periodic Table Group 1 elements (Li, Na, K, Cs, Rb) are soluble.
2	Salts containing NH_4 ammonium ion and nitrate and nitrite ions (NO, and NO_2) are generally soluble.
3	Most salts of Cl, Br, and I (halide salts) are soluble. Except for Ag, Pb^{+2} and Hg_2.
4	Silver salts of $AgNO_3$ and Ag ($C_2H_3O_2$) are soluble. All other silver salts are insoluble.
5	$CaSO_4$, $BaSO_4$, $PbSO_4$, Ag_2SO_4, and $SrSO_4$ are insoluble, but most other Sulfate salts are soluble.
6	Hydroxides: Group 1 metals are soluble; Group II metals are slightly soluble; Salts of transition metals and Al^{+3} are insoluble. Reactions of $Al(OH)_3$, $Fe(OH)_3$, and $Co(OH)_2$ are also insoluble.
7	Group II carbonate salts are insoluble, as are most other carbonates.
8	Sulfide salts are insoluble: CdS, FeS, Ag_2S, As_2S_3, Bi_2S_3, PbS are also insoluble.
9	Reactions of chromates with cations often yield insoluble salts.
10	Fluoride reactions with Group II metals will often yield insoluble salts, except Calcium Phosphates are also frequently insoluble.
11	Phosphates are also frequently insoluble.

Soluble metal salts have been used as colorants in ceramic art by many artists such as Gary Holts, Arne Ase, John Shirley, A. Feyza Cakir Ozgundogdu and others due to the diverse and unique color tones they provide. John Shirley and A. Feyza Çakır Özgündoğdu have investigated the potential uses of water-based colorants possessing characteristic color and depth properties in porcelain forms in their studies (Özgündoğdu, 2009). In their study, Sarıoğlu and Güner examined the colors and effects created by 31 different chemicals, most of which are metal salts and soluble in water, on ceramic structures (Sarıoğlu and Güner, 2010).

Due to their water-solubility, these metals create different color and texture effects on the clay surface through a unique interaction, diffusing onto the surface. Additionally, even when used as a component in glaze, they enable us to achieve different decorative effects in underglaze and overglaze applications.

As examples of soluble metal oxides used in artistic applications; Copper Chloride ($CuCl_2$), Copper Sulphate ($CuSO_4$), Potassium Dichromate ($K_2Cr_2O_7$), Nickel Chloride ($NiCl_2$), Sodium Chromate (Na_2CrO_4), Copper (II) Nitrate Trihydrate $Cu(NO_3)_2 3H_2O$, Cobalt (II) Nitrate Hexahydrate ($Co(NO_3)_26H_2O$), Iron Chloride ($FeCl_3$), and Bismuth Nitrate ($Bi(NO_3)_3$) can be listed (http 2; Özgündoğdu, 2009; Güzelgün, 2010; Ase, 1989).

2. EXPERIMENTAL STUDIES AND ARTISTIC PRODUCTIONS

The effects of four different metal salts (Table 2) on the surfaces of artistic glasses produced using the hot glass technique have been investigated within the scope of the study.

The designed glasses were produced in 2 stages. In the first step, glass samples in the form of plates were prepared, metal salts were applied to them, and a preliminary firing was applied to these pieces. In the second step, the glass plates, annealed and metal salt applied, were transferred to the surfaces of the forms produced with the hot glass blowing technique with a hot application and integrated with the form with a patchwork approach.

Table 2. *List of used metal salts.*

	Name of the Metal Salt	Composition
1	Cobalt (II) Nitrate Hexahydrate, 99%	$Co(NO_3)_26H_2O$
2	Chromium (III) Nitrate Nonahydrate, 99%	$Cr(NO_3)_39H_2O$
3	Copper (II) Nitrate Trihydrate, 99%	$Cu(NO_3)_23H_2O$
4	Nickel (II) Chloride, 98%	$NiCl_2$

In plate production, “Cristalica Studio Glass” imported from Germany and “Glasma 705” glass produced in Sweden were used. 45 plates with dimensions of 100x100x10 mm were produced. In the hot glass studies, a Pika brand S-40 model “Slovenia” production electric-powered crucible glass melting furnace was used. After the annealing process, metal salts were applied to the surfaces of the produced plates, and then the plates were subjected to heat treatment at 2 different temperatures, 900 ^{0}C and 1000 ^{0}C, in the fusion furnace of the Pika brand GL-V model. The plates have been prepared in two different ways, using and not using the ground color, in order to achieve different effects.

2.1. Production Stages of Glass Plates

To produce glass plates, the glass that is molten in the furnace (1200 ^{0}C) is taken by turning it full circle on the end of a pre-heated steel blowpipe and several layers of glass are wrapped after the pipe cools down to the desired dimensions.

Then, the glass taken from the furnace is poured through the pipe perpendicularly onto the pre-heated metal table, maintaining its temperature.

After the glass is poured vertically onto the table, it is quickly turned to make it parallel to the table plane and break away from the steel pipe. If the glass does not break, the glass should be removed from the pipe with the help of flat-blade scissors or round-blade scissors. The poured glass is heated with a gas blowtorch or oxygen blowtorch when necessary, and the heat distribution on the surface is made homogeneous (Figure1).

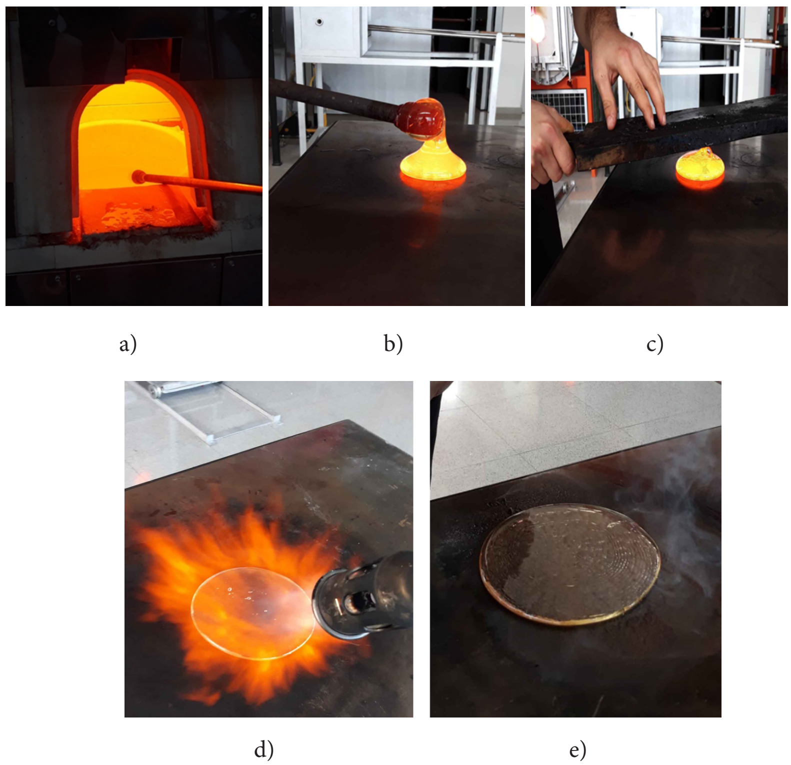

Figure 1. *Glass plate production stages a) Removing the glass from the furnace b) Flowing the glass taken from the furnace c) Shaping with the help of wood d) Homogenization with the help of a blowtorch e) Plate ready for annealing.*

The final stage in glass plate production is the annealing process in order to relieve the stresses in the glass structure (Table 3).

Table 3. *Annealing furnace diagram.*

Heating Rate	Temperature	Holding
Skip	505˚C	8 hours

Structurally, the glass surface, being very smooth, has been abraded through sandblasting to obtain a more matte and rougher surface, allowing metallic salt mixtures to adhere more easily.

2.2. Application of Metal Salts on Glass Surface

Acros brand 99% purity Cobalt (II) Nitrate Hexahydrate, Chromium (III) Nitrate Nonahydrate, Copper (II) Nitrate and 98% purity Nickel (II) Chloride were used. The metal salts, which were in the form of large granules, were crushed in a mortar with the help of a pestle and turned into powder. The salts were weighed in the range of 10-15 g and placed in the crucible. Then, 10 g of wallpaper glue was added to the composition to ensure that the salts adhere to the glass. To ensure that the metal salts mixed with the wallpaper glue and to dissolve the salts, approximately 20 to 25 ml of water was added to the mixture, mixed with a brush, and quickly applied to the surface before the glue hardened. To obtain different colors and textures, metal salt mixtures were applied to plate glass in two ways: directly and using ground color. “Kugler Colors” brand white and blue glass powder was preferred as the ground color (Figure 2).

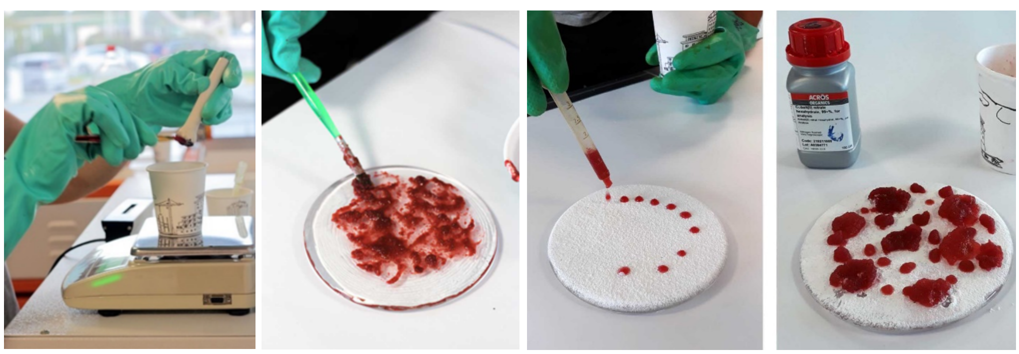

Figure 2. *Application of metal powders to glass plates produced without and using ground color.*

The plates to which the mixture was applied were fired according to the determined heat treatment in the fusion furnace (Table 4), and the effects of the heat treatment carried out at 2 different temperatures on the final product were examined.

Table 4. *Fusion furnace thermal diagram*

	900 ˚C		1000˚C	
	1	2	1	2
Rise	90 ˚C	Skip	90˚C	Skip
Temperature	900 ˚C	30 ˚C	1000˚C	30 ˚C
Hold	5 minutes	-	10 minutes	-

3. RESULTS AND DISCUSSION

Images of the glasses obtained after applying different metal salts to plates obtained without and using ground color are presented in Figure 3.

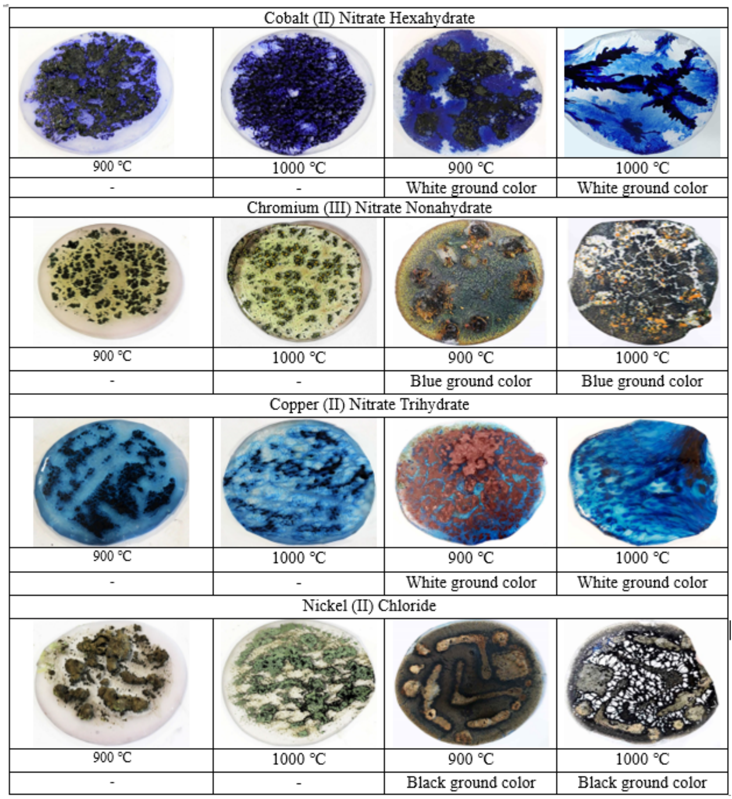

Figure 3. *Surface properties of glass plates treated with metal salt after firing.*

According to obtained results, in the applications made with Cobalt (II) Nitrate Hexahydrate, it was observed that a more homogeneous distribution and a stronger reaction with the glass surface occurred on the glass plate surface baked at 1000 ^{0}C . The brightness, color effect and distribution on the surface of the plates on which white ground color is applied are stronger than the plates without ground color.

It was observed that metal salts clumped on the glass surfaces obtained with Chromium (III) Nitrate Nonahydrate at 900 ^{0}C without applying ground color and did not create a homogeneous color effect. At 1000 ^{0}C, it is seen that a brighter surface effect and vibrant yellows as a color tone and the black spots surrounding them are formed in the form of gatherings. It has been observed that Chromium (III) Nitrate Nonahydrate swells on the glass plate surfaces produced using blue background color. A greenish-yellow tone contour effect occurred on the surface, and it was determined that it did not form a glassy layer, taking on a completely matte appearance.

On the surfaces obtained by Copper (II) Nitrate Trihydrate, strong copper-colored moires resembling the appearance of craters were observed on the plate fired at 900 ºçusing a white background color. In the other three plates, surfaces in light and dark blue tones that integrate with the glass surface, have high brightness and strong color effects are obtained.

When the glass surface to which Nickel (II) Chloride was applied was fired at 900 ^{0}C, no homogeneous distribution was observed on the surface. At 1000 ^{0}C, the metal salt layer integrated with the glass body and a shiny surface with a black outer contour was obtained under green crater-like tones. In the application using black background color, it was observed that as the temperature increased, the surface turned from matte to shiny and coppery colors were formed.

4. PERSONAL APPLICATIONS

Glass plates obtained with the use of metal salts were applied to the works produced with the hot glass blowing technique. Images of the designs are presented in Figure 4.

Figure 4. *Designs made by the author (Emir Özkaya).*

For the production of the designed artistic glasses, first the glass taken from the furnace was blown, then cooled for a certain amount of time, and then powder color coating in different colors was applied to the surface of the second layer of glass taken from the furnace. Wet newspaper was used as an auxiliary material during the shaping processes.

The glass, which was brought to the appropriate temperature in the Glory Hole furnace, was given a flat form. Then, a hole was drilled in the center of the glass with the help of a hard drilling tool (Figure 5).

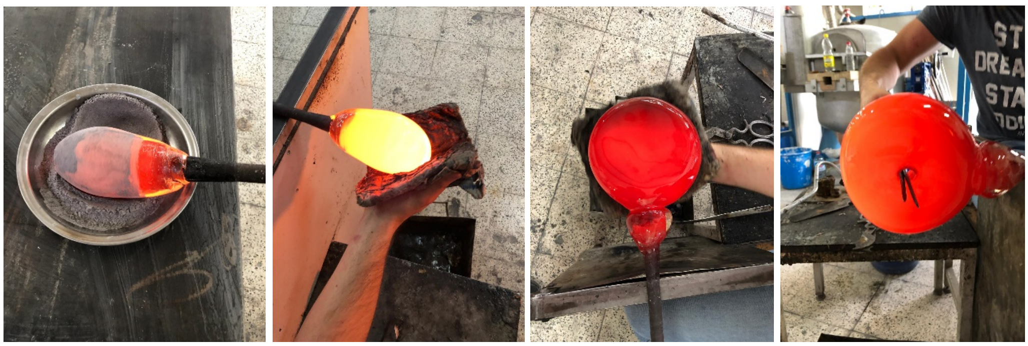

Figure 5. *Powder color coating and forming process.*

After the shaping process, the piece produced by blowing on the tip of another pipe was added to the first piece, provided that the tip was hot. After the integrated part reached the same temperature as the body, heat homogenization was performed once again in the glory hole furnace and the produced work was subjected to the annealing process according to the diagram given in Table 3. Afterwards, the resulting form was combined with a decorative effect plate with a patchwork approach.

Photos of the obtained artistic glasses are presented in Figures 6-9.

Figure 6. *"Hierarchical Impressions" Study with Cobalt Nitrate (Photographed Emir Özkaya).*

Figure 7. *"Hierarchical Impressions", Chromium Nitrate application (Photographed Emir Özkaya).*

Figure 8. *"Hierarchical Impressions 6", study done with Copper Nitrate (Photographed Emir Özkaya).*

Figure 9. *Studies Conducted with Nickel Chloride (Photographed Emir Özkaya).*

5. CONCLUSION

The way to obtain original works in glass art through a contemporary approach involves the use of innovative ideas, materials, and techniques. The use of new materials involves a series of experimental and application processes. Within the scope of the study, the possibilities of using water-soluble metal salts, which have been applied in ceramic bodies and glazes in the past and today, in artistic glass production were investigated.

In order to ensure that the metal salts used in the experiments spread more homogeneously on the glass surface, grain sizes were reduced with the help of a porcelain mortar. Wallpaper glue was used as a thickener so that the salts could be easily applied to the glass surface and remain stable on the surface. In order to obtain different decorative effects, the amount of metal salt, water and thickener used, and the oven temperature were determined as variable parameters. In addition, metal salts were applied in two different ways: direct application on glass plates and application after using the ground color. It was tried to increase the effect of the colors and textures obtained by creating ground color contrast on the glass plates. Each metal salt mixture revealed different decorative color, texture and distribution effects on the obtained surfaces.

In the experiments carried out at 900 ^{0}C, it was observed that the mixtures applied remained in the form of powder on the glass surfaces, swelled and formed crater-like shapes. It has been determined that the mixtures are not suitable for heat treatments at 900˚C in terms of usage possibilities because they remain on the surface. For this reason, applications were made at higher temperatures and the results were examined. In experiments carried out at 1000 ^{0}C, it was observed that metal salts showed higher dispersion on the glass surface and exhibited different color and texture properties. Color transitions, textural and formal approaches similar to the watercolor effect were achieved. Decorative effects that allow original and artistic uses have been achieved.

With this study, unique and individually different possibilities have been opened with decorative uses obtained through experimental processes, and an option has been successfully created for innovative and original uses of glass regarding working with alternative materials in glass surface decoration applications.

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