Densification, Crystallization, and Sticking Behavior of Crushed Waste Glass Sintered in Refractory Molds with Release Agents

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FINAL

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1. INTRODUCTION

Ceramic products, such as tile, are currently processed from recycled waste glass by sintering crushed glass in refractory molds. This processing method utilizes the unique low temperature viscous phase sintering characteristic of glass particles. The development of this method has been limited by processing problems of crystallization of the glass and sticking of the glass to molds. Release agents have been used, but sticking problems still occur.

This report documents research performed to provide an understanding of the crystallization and sticking problems that occur when sintering recycled glass in refractory molds coated with release agents. Background information and a review of the related literature are presented in the next section. The experimental procedure used to investigate these problems is then discussed in Section III. The results of the experimental work are presented in Section IV, followed by a summary, conclusions and recommendations for future work in Sections V and VI.

2.0 BACKGROUND INFORMATION AND LITERATURE REVIEW

2.1 Commercial Soda-Lime Glass

Over 95% of commercial glass consists mainly of sodium, calcium, and silicon oxides (Na_2O, CaO, and SiO_2), referred to as soda-lime glass [1]. Alumina, magnesia, and several other oxides are also included as minor constituents. Soda-lime glass has the unique combination of low cost raw materials with good glass manufacturing characteristics. Soda-lime glasses generally fall in a narrow range of compositions along the boundary between devitrite (Na_2O-3CaO-6SiO_2) and tridymite (SiO_2) in the Na_2O-CaO-SiO_2 phase diagram. Variations from this narrow range can adversely affect various important characteristics, such as the glass melting behavior, crystallization tendency, glass workability, and chemical durability.

The compositions of most container and plate glass is fairly similar, but slight variations in colorants and the ratios of the constituents can have a significant affect on some properties, such as thermal expansion and crystallization behavior. If recycled glass from different sources is combined, these variations can cause problems depending on the processing methods used. Processing problems from variations in composition can generally be reduced by using finer glass particles. The particle size of the glass used to make recycled glass products can also have a significant affect on the densification, crystallization, and sticking behavior as discussed in more detail in the following sections.

The primary use of recycled soda-lime glass is as cullet in the manufacture of new glass products. A variety of secondary uses have also been developed [2,3]. A limited amount of research has been conducted in the use of recycled glass as a raw material in ceramic products other than glass, and has been described in publications [4-16] and patents [17-24]. The crystallization, surface tension, and wetting behavior of soda-lime glass compositions have been investigated for many years [25-43], and is reviewed in the following sections

2.2 Viscous Flow and Densification of Glass Particles

Glass is a noncrystalline solid, which means that it only has short-range crystal structure. The bond angles between atoms in a glass structure vary over a range of angles. This is in contrast to a crystalline structure, which has long-range order and fixed bond angles. The periodic structure of a crystalline material leads to a melting temperature, where a sudden transformation occurs between a liquid and solid. Glass does not melt at a particular temperature like a crystalline material. The variations in bond angles causes the glass structure to soften over a range of temperatures. The viscosity changes gradually over this range, which allows glass to be formed into a wide variety of products. Normally glass products are formed while cooling from the melt, but as discussed in this report glass particles can be fused together by heating the glass until the viscosity decreases sufficiently.

Fusing glass particles into a dense product occurs by viscous phase sintering at temperatures much lower than the melting temperatures of crystalline materials of the same composition. This sintering mechanism is controlled by glass composition, impurities, surface area, packing efficiency, and crystallization behavior. Some glass compositions densify easily by viscous phase sintering, while other compositions do not densify well. The viscosity has to decrease sufficiently for glass flow to occur, but not too rapidly to cause crystallization. If crystallization occurs, the viscosity will increase and further densification will be inhibited. Impurities or additions of crystalline materials to the glass particles will also adversely affect the sintering behavior.

The driving force for viscous phase sintering of glass particles is the reduction of surface area. Increasing the surface area will tend to promote sintering. The surface area is increased by decreasing the particle size.

Another important parameter that affects viscous phase sintering is how well the particles are initially packed together. Increasing the packing density promotes sintering. Ceramic manufacturing normally involves forming methods, such as extrusion, pressing, and slip casting, which result in relatively high green densities. This is critical when sintering crystalline raw materials into dense fired articles. Pouring glass particles into a refractory mold is not a very efficient method of achieving densely packed particles. However, there are methods of increasing the particle packing, such as increasing the particle size distribution, reducing particle size, and shaking or tapping the molds.

Sintering can also be enhanced by additions of low melting glasses or fluxes. These additives can promote viscous flow and sintering, but usually also increase the cost and complexity of the materials system. Combining materials to produce a multiphase composite system allows unique combinations of processing and properties to be achieved which are sometimes not possible with single phase systems.

Glass softening and viscous flow are required for densification of glass particles, but also lead to sticking and crystallization problems as discussed in the following sections.

2.3 Sticking Behavior of Glass at High Temperatures

Glass softening and flow is required for glass particles to sinter together into a dense product, and to produce a smooth surface. However, this also causes the glass to tend to stick to materials that come in contact with the glass, such as a refractory mold or even a release agent. For sticking to occur, the glass has to wet the surface of the material it is in contact with. This is similar to a liquid wetting a solid, which is controlled by the differences in surface tensions (or surface energies) between the materials.

Surface tension is the energy required to increase the surface of an interface by a unit area. A liquid (or glass) on a solid surrounded by a vapor involves three surface tensions at the liquid-solid, liquid-vapor, and solid-vapor interfaces. Wetting of the surface is controlled by the differences between these surface tensions. For a liquid to wet and spread across a solid, the liquid-vapor surface tension has to be less than the solid-vapor surface tension. The difference between these surface tensions also has to be greater than the solid-liquid surface tension. With these conditions satisfied the liquid will spread across the solid to lower the overall energy of the system. This means that for applications where you want a liquid to wet a surface, such as glazing a ceramic, the surface tension of the liquid should be less than that of the solid (referring to the vapor related surface tensions). Glasses usually have low surface tensions, and so wet most surfaces easily.

Sintering crushed glass in a refractory mold coated with a release agent is an example of where wetting is not desirable. In this case the surface tension of the glass should be higher than that of the release agent. This is a problem because glasses have relatively low surface tensions, and there are only a limited number of materials with even lower surface tensions. A further complication of the problem is the dynamic behavior of the surface tension of glasses. During heat treatment the surface tension of a glass will decrease with time, because constituents that lower the surface tension will diffuse to the surface.

The surface tension of glass varies with composition. Silica by itself has a low surface tension, which can be increased or decreased with different additives. Soda-lime glass compositions have surface tensions slightly higher than silica [39], and thus silica is a potential candidate for use in a release agent. There is only limited data available on the surface tension of glasses and other materials [44, 45]. Boron and phosphorous oxides (B_2O_3 and P_2O_5) stand out as having very low surface tensions, but the low melting temperatures of these oxides eliminates their use as release agents.

The firing atmosphere can also affect the surface tension of glass [39]. Polar gases, such as water vapor, have been shown to significantly lower the surface tension of soda-lime glass [39]. This indicates that firing in moist air will lower the surface tension and cause glass to stick more severely than firing in dry air.

There are also many other factors that are important for release agents in addition to the surface tension, such as: the rates of reaction and dissolution into the glass; refractoriness; bonding of the release agent to the mold; bonding between particles within the release layer; and stability on repeat firings. The rates of reaction and dissolution of a release agent are controlled by the rates of ion transfer across the interface and diffusion into the glass. These rates vary greatly between different materials. A good release agent should have low rates of reaction and dissolution.

There are many factors that affect these rates, one of which is the refractoriness of the release agent. The release agent should have a high melting temperature, and not form low melting phases when combined with the glass. Refractory materials have very strong atomic bonding, which will tend to resist dissolution and diffusion into a glass.

The characteristics of the release coating can also have a significant affect on the sticking behavior of glass, especially when some limited degree of sticking occurs. The release should be bonded well to the refractory mold to keep the release from separating when some sticking occurs. How well the release particles are bonded together is also an important factor in the performance of the release. If no sticking occurs, then ideally the release particles should be strongly bonded together. However, if sticking occurs, then weakly bonded release particles will limit the amount of release that sticks, and extend the number of repeat firings possible. The strength of the refractory mold may also be important. Ideally the weakest link should be as close as possible to the glass-release interface. A final factor that may be important is the stability of the release on repeat firings. Reactions and phase changes in the constituents of the release can occur during repeat firings. The release should be designed to limit adverse changes that would degrade the release performance.

Commercial release agents, referred to as kiln washes and shelf paints, are commonly used for firing clay based materials. Liquid phases form during the firing of these materials, and release agents are needed to prevent sticking to the refractories. These releases work well because the requirements of firing clay based materials are not very demanding. Fusing glass has much more potential for sticking problems, especially when low-melting fluxes are included. The optimum release for glass may be different than that for clay based materials.

Commercial release agents are typically made from mixtures of alumina hydrate and kaolin, or silica and kaolin. [46, 47] Kaolin and alumina hydrate decompose during firing. Phase changes and reactions also occur. Kaolin is mainly composed of kaolinite (Al_2O_3-$2SiO_2$-$2H_2O$). Alumina hydrate is composed of gibbsite- (Al_2O_3-$3H_2O$). Both kaolinite and gibbsite decompose on heating when the chemically absorbed water is evolved. Hygroscopic or ‘free’ water (not chemically adsorbed) is removed by about 212F (100C), and can result in weight loss of a few percent. Chemically adsorbed or 'combined' water evolves from kaolinite from about 750-1100F (400-600C), and results in a 14% weight loss. The chemically combined water in gibbsite evolves around 570F (300C), and results in a 35% weight loss. A series of phase changes and reactions occur at higher temperatures, especially when both are combined together. Kaolin and silica mixtures will also react and change during firing. If a release continues to change on repeat firings, then this may have an affect on the performance of a release.

For this project alumina hydrate, silica, and kaolin were chosen for investigation as release agent constituents for use with soda lime glass. These materials provide significant variations in the critical parameters discussed above. Alumina and silica are very refractory oxides, and represent extremes in surface tensions. Alumina has a substantially higher surface tension than soda-lime glass, while silica has a slightly lower surface tension. Alumina and silica also have large differences in reaction and dissolution rates with glasses. Silica tends to dissolve in glasses faster than alumina. Thus, silica and alumina each have advantages and disadvantages. Kaolin will also be included to provide plasticity, which will help bond the release agent particles together and to the mold.

2.4 Crystallization of Glass

Glass is metastable and will transform to the stable crystalline state if enough thermal energy is available. This transformation is called devitrification or crystallization, and occurs by a two step nucleation and crystal growth process. As glass is heated the viscosity decreases, which increases the tendency for structural rearrangement and crystallization. When the temperature is increased high enough (usually just above the softening point), crystal nuclei begin to form. The nuclei are simply tiny regions in the glass structure where the crystalline structure has formed. As the temperature is further increased the rate of nuclei formation, or nucleation, increases to a maximum at some temperature, depending on the composition. At higher temperatures additional thermal energy causes the nuclei to grow by crystal growth mechanisms. The rate of crystal growth increases with increasing temperature to a maximum at some temperature, and then the rate decreases to zero at the liquidous temperature.

Nucleation can occur homogeneously or heterogeneously. Homogeneous nucleation is random nucleation without preferential sites in a homogeneous material. Heterogeneous nucleation occurs from preferred sites, such as surfaces, grain boundaries, second-phase particles, etc. Heterogeneous nucleation dominates, because there are always defects and impurities present. Nucleation and crystal growth can occur within bulk glass or on the surface; referred to as bulk crystallization and surface crystallization. Most commercial glass compositions tend to crystallize mainly on the surface, because of the heterogeneities on the surface. Dust has even been shown to greatly enhance surface crystallization of soda-lime glass [34].

When glass is crushed and milled into finer and finer particles, the surface area greatly increases. The surface area of a typical glass container increases by about 77 times when the glass is crushed to 30 mesh, and about 150 times when reduced to 50 mesh. The original surface area of the container in these cases represents only about one percent of the surface area of the crushed glass. This indicates that the new surface created from crushing will dominate the crystallization behavior.

The new surface that is created from crushing glass is covered with broken chemical bonds. This makes the surface highly reactive, and thus it will react and bond to anything that will satisfy these broken bonds, especially water vapor. Because of this highly reactive surface, variations in surface chemistry easily occur from changes in processing and storage conditions. The surface chemistry (what is bonded to the surface) can have a significant affect on how the particles crystallize, and also affect the sintering and sticking behavior.

Sintering glass particles or powder into a dense material usually results in a microstructure that still retains interfacial regions between the particles. These interfacial regions tend to crystallize similar to the surface. This results in crystallization throughout the material, similar to bulk crystallization. As the particle size is decreased the rate of crystallization increases and the crystallization temperatures decrease. Because of this, a coarser particle size will reduce the tendency for crystallization. However, the glass composition, surface chemistry, and firing conditions are also very important in controlling the crystallization behavior.

Commercial soda-lime glass compositions used to manufacture containers and plate glass are designed to not crystallize during the typical glass forming operations, where the glass is rapidly cooled and formed from the melt. Small additions of oxides, such as alumina and magnesia, are used to further limit the tendency for crystallization. Soda lime glass will crystallize when reheated to a high enough temperature and long enough hold time. The initial temperature of crystal growth for a soda lime glass was found to occur at about 1380F (750C), with the maximum rate of crystal growth at about 1780F (970C) [34]. The crystallization occurred on the surface. The crystal growth temperatures will vary depending on the actual soda-lime composition, and surface chemistry. These results show that soda-lime glass will crystallize at relatively low temperatures, which may be difficult to avoid at the temperatures required to sinter crushed glass in a loosely filled mold.

2.5 Summary of the Sticking and Crystallization Problems

Sintering crushed glass requires firing conditions to promote glass flow and a decrease in viscosity. Reducing the particle size and increasing packing density will enhance the sintering mechanisms. Unfortunately, glass flow and lowering viscosity also lead to sticking and crystallization problems. If the materials system (soda-lime glass) is fixed, then the ability to produce a dense product without sticking and crystallization problems is dependent on the processing method used. The purpose of the experimental work presented in the following sections is to develop an understanding of the current practice of sintering crushed glass in refractory molds with release agents, and to determine if a processing window exists where a satisfactory product can be produced.

3.0 EXPERIMENTAL PROCEDURE

3.1 Introduction

This section describes the experimental procedures that were used to investigate the sticking and crystallization problems that currently occur when sintering crushed glass in refractory molds with release agents. The research was divided into two main phases, as discussed in the next two sections. The first phase focused on the sticking behavior, and the second phase on crystallization.

To reduce the number of variables involved, a single glass source was used throughout the investigation. TriVitro #40 crushed waste glass (TriVitro Co., Seattle, WA) was chosen, because it is representative of the type of glass that is commonly used, and is commercially available. This glass consists of recycled "deadleaf" green glass bottles crushed to between 30 and 50 mesh. The glass was relatively free of paper and other contaminants, and was used in the fusing studies as received.

The TriVitro glass composition was determined by x-ray fluorescence (XRF) at the Mineral Lab, Inc. (Lakewood, CO). For the XRF analysis, the glass was milled to <400 mesh in a tungsten carbide swing mill (to avoid Fe contamination). 31 major, minor, and trace elements were analyzed with relative precision/accuracy of 5-10% for major-minor elements and 10-15% for trace elements (those listed in ppm). A replicate sample and standard reference material were also run. The results are presented in Section IV.

A standard firing profile (from R. Kirby, CWC) was used for all firings in the research with only the maximum temperature (Max Temp) and hold time (MT hold) varied. This firing profile is listed in Table I. All firings were conducted in a Skutt KM-714 automatic kiln (Portland, OR). The Max Temp was varied from 1300 to 1700F, and the MT hold varied from 5 minutes to 10 hours, as discussed in the following sections.

Table I - Standard Firing Profile

- 500F/hr to 1100F, with 20 min hold
- 500F/hr to Max Temp, with MT hold
- Natural Cooling (programmed at 9999F/hr) to 1020F, with 15 min hold
- 70F/hr to 950F, with no hold time
- 300F/hr to 250F, with no hold time

3.2 Release Agent Study

Research was performed to develop an understanding of the sticking behavior of release agents composed of alumina hydrate, silica, and/or kaolin. Comparisons were also made with commercial release agents. The alumina hydrate, silica (<325 mesh), and kaolin (EPK) were from Creative Ceramics (Santa Rosa, CA). The following four commercial releases were evaluated: Mile Hi Ceramics kiln wash (Denver, CO); Seattle Pottery Supply shelf paint (Seattle, WA); Hot Line Hi Fire shelf primer and Thin Fire shelf paper (both from Sundance Art Glass Center, Mountain View, CA).

Sixteen mixtures of alumina hydrate, silica, and kaolin were investigated. The compositions in weight percent are listed in Table II. Three ratios of alumina hydrate to silica were used: 100/0, 50/50, and 0/100. These were combined with five kaolin percentages: 0, 25, 40, 50, and 75%. The sixteenth composition consisted of 100% kaolin. The other two end members were also included: composition 1 was 100% alumina hydrate, and composition 3 was 100% silica.

Table II - Release Agent Compositions

Comp. #	Alumina/Silica	Alumina (%)	Silica (%)	Kaolin(%)
1	100/0	100	0	0
2	50/50	50	50	0
3	0/100	0	100	0
4	100/0	75	0	25
5	50/50	37.5	37.5	25
6	0/100	0	75	25
7	100/0	60	0	40
8	50/50	30	30	40
9	0/100	0	60	40
10	100/0	50	0	50
11	50/50	25	25	50
12	0/100	0	50	50
13	100/0	25	0	75
14	50/50	12.5	12.5	75
15	0/100	0	25	75
16	100/0	100	0	100

These 16 release combinations, along with the commercial releases (excluding the Thin Fire shelf paper), were mixed with water into slurries for application on refractory molds. A weight ratio of 5 parts release powder to 8 parts water was used. This is equal to a volume ratio of 1 part release to 4 parts water (assuming densities of 2.5 and 1.0 g/cc for the release powder and water, respectively). Compositions 1-3 without kaolin did not disperse well in water, and so 1 weight % CMC gum binder (from Creative Ceramics, Santa Rosa, CA) was also added. The slurries were thoroughly mixed, and then brushed on the refractory molds in four layers. Each successive layer was brushed on perpendicular to the previous layer.

Two sizes of refractory molds were used; 4 in x 4 in, and 6 in x 6 in. The 4x4 molds produced single square tile samples. The 6x6 molds were divided into 9 square 1.75 in x 1.75 in sections, and thus produced nine samples. This allowed nine different releases to be tested with one mold. The molds were obtained from R. Kirby of CWC.

After applying the release, the molds were dried at 140°F in an oven. The release coated molds were then either filled with crushed glass, or first prefired before filling. The prefiring profile consisted of: 500°F/hr to 1100F, with a 20 min hold; 500F/hr to 1800°F; and then natural cooling with the power turned off. The 4x4 molds were filled with 250g of glass. Each of the nine sections of the 6x6 molds were filled with 10g of glass. The glass filled molds were fired by the standard firing profile (Table I) to various maximum temperatures and hold times.

A semi-quantitative rating system was used to evaluate the release performance, as listed in Table III. Examples of each rating level were used as standards for relative comparisons. Ratings of 1.5, 2.5, 3.5, and 4.5 were also used to further distinguish the differences in performance. The experimental error in ratings is estimated to be < 0.5 of a rating point. The releases were also evaluated after repeat firings, without recoating the release, and with new glass filled in the molds after each firing.

Table III - Semi-Quantitative Release Agent Rating System

Rating	Description
1	No sticking
2	Slight sticking visible
3	Moderate sticking
4	Severe sticking, without much sticking on sides of sample
5	Severe sticking, including sides

3.3 Crystallization Study

The crystallization behavior of the glass was investigated by visual inspection of fired samples with and without an optical microscope, and with x-ray diffraction. Two thicknesses of TriVitro glass samples were prepared in the 6x6 molds by filling the sections with either 5 or 10 grams. The crystallization behavior of bulk samples of clear, green, and amber glass containers were also studied for comparison. Broken pieces of the glass with > 1 cm dimensions were used. The samples were fired according to the standard firing profile (Table I) to various maximum temperatures and hold times.

Visual inspection without a microscope was used to observe the presence of a hazy appearance indicating surface crystallization. Inspection at 40x, 100x, and 400x with an optical microscope was then used to observe the presence of crystallites. By varying the thickness (with either 5 or 10 gram samples) the intensity of transmitted light was varied to observe crystals on the surface or in the interior of samples. The crystallization behavior was also correlated with the densification of the samples and smoothness of the surfaces. The goal was to determine if dense samples could be produced with a smooth surface without crystallization.

Fired samples were also milled to < 400 mesh for x-ray powder diffraction analysis by the Mineral Lab, Inc. (Lakewood, CO). The diffractometer scanned from 3-61 degrees two-theta with 0.02 step size using Cu-Kα radiation. The resulting x-ray diffraction patterns were analyzed to determine the phases that crystallized.

4.0 RESULTS AND DISCUSSION

4.1 Introduction

The experimental work that was conducted provides an understanding of the densification, sticking, and crystallization behavior of soda-lime glass fired in refractory molds with release agents. The results are specific to the particular glass studied, but some general conclusions can also be made. The procedures used for the experimental work were described in the last section. The results are divided into the release agent and crystallization studies, and presented in the following two sections.

The chemical analysis of the TriVitro glass is presented in Table IV. The results are the averages of two sets of measurements. The composition consists mainly of SiO_2, Na_2O_3, and CaO with minor amounts of Al_2O_3, K_2O, MgO, and Fe_2O_3. The amount of MgO is relatively low for commercial soda-lime glass. Low MgO content will tend to increase the tendency of the glass to crystallize.

4.2 Release Agent Results

The TriVitro glass was initially fired at a series of maximum temperatures ranging from 1400 to 1700F to determine suitable firing conditions for the release study. These firings were conducted with Mile Hi kiln wash coated on 4x4 molds. The standard firing profile (Table I) with a maximum temperature of 1580F and 5 minute hold was selected for use in all firings of the samples with results presented in this section of the report. These firing conditions produced dense samples with a smooth surface and rounded edges.

Table IV - Chemical Analysis of the TriVitro Glass

Oxide	Wt %	Element	ppm	Element	ppm
SiO_2	71.3	S	<500	As	<20
Na_2O	13.4	Cl	<200	Y	14
CaO	11.1	Cr	182	V	12
Al_2O_3	1.78	Sr	148	Zn	12
K_2O	0.73	Zr	68	Ni	10
MgO	0.44	Sn	<50	Cu	<10
Fe_2O_3	0.14	U	28	Mo	<10
P_2O_5	<0.05	Pb	24	Th	<10
BaO	0.04	Rb	24	Nb	<10
TiO_2	0.03				
MnO	<0.01				

A release agent should be easy to apply and should form a good coating, in addition to preventing glass from sticking during firing. These additional requirements varied greatly between the 16 compositions that were investigated in the alumina hydrate, silica, and kaolin system. Table V summarizes the results for these compositions along with the commercial release agent results. The alumina/silica ratio and the weight percent kaolin are listed, followed by evaluations of the ease of application and quality of the coating. The last column in the table gives the release ratings after one firing based on the system given in Table III. Ratings of 3 and above indicate unacceptable sticking, while ratings of 2 and below are considered acceptable. Ratings from 2 to 3 are borderline between acceptable and unacceptable, and would depend on the particular application.

Compositions 1-3, all without kaolin, had problems causing these compositions to be unacceptable for use as release agents. Composition 1 which consisted of 100% alumina hydrate was very difficult to mix with water and spread in a uniform layer. The dried release coating of this composition was also powdery and of poor quality. Composition 2 was better than composition 1, but still resulted in poor ease of application and quality. Composition 3, which consisted of 100% silica, was easier to apply, and produced a good initial coating.

After firing, all three of these compositions stuck severely to the glass with release ratings of 4 to 4.5. The powdery nature and poor bonding of the release coatings resulted in large amounts of release sticking to the glass samples. Most of the release could be washed and brushed off. The remaining amount of stuck release was much greater for composition 1 compared to composition 3, and an intermediate amount remained stuck to composition 2. These results indicate that alumina sticks and bonds to glass more than silica, which correlates with the greater surface tension of alumina compared to silica. However, as shown later in this section, alumina results in better repeat firing results than silica, which may be related to the greater diffusion of silica in glass than alumina.

The results of compositions 1-3 demonstrate the importance of kaolin, or some type of clay, as a component of the release agent to provide bonding within the release coating. Composition 16, consisting of 100% kaolin, mixed and suspended well in water, and was easy to apply. However, after drying the release coating cracked, because the particles were bonded too strongly together and the shrinkage was too great. Compositions 13-15, with 75 wt % kaolin also resulted in similar results, and thus none of these compositions were further investigated. Kaolin is needed as a component, but too much results in cracking problems.

Compositions 4-12, with 25 to 50% kaolin, applied easily with good quality coatings. The compositions with greater alumina tended to be more powdery than those with greater silica. After firing, all of these compositions resulted in acceptable release ratings of 1.5 or 2. A difference of 0.5 in these ratings is probably within the experimental error, and should not be considered a significant difference.

The commercial release agents all applied easily, and produced good coatings, except for the Hot Line Hi Fire shelf primer which cracked after drying. Even drying slowly at room temperature resulted in cracking. The cracking did not affect the release rating which was 1.5 after one firing; the same as the Mile Hi Ceramics and Seattle Pottery Supply release agents. Applying the thin fire shelf paper only required cutting it into the desired shape and placing it in the mold. After firing, the fiber paper transformed into powder and severely stuck to the glass with a rating of 5, the worst performance of any of the releases studied.

Compositions 4-12 and the first three commercial releases listed in Table V were selected for further study with repeat firings. In Figures 1-3 the release ratings are plotted versus the number of firings for compositions with 25, 40, and 50% kaolin. The data plotted are for running averages of five data points to smooth out the variations in the data that resulted from only assigning ratings every one-half point. When a composition degraded to the point where the refractory mold was showing through the release layer, typically with ratings of 3.5 to 4, then glass was not refilled in the mold section with that composition for additional firings.

The three curves in Figures 1-3 are for compositions with different alumina/silica ratios. The data in all three figures show that the compositions containing silica, but no alumina (0/100 alumina/silica ratio), degrade much more rapidly on repeat firings than the other compositions. With 25% kaolin (Figure 1) composition 5 with a 50/50 alumina/silica ratio degraded less than the other two compositions out to nine firings. With 40 and 50% kaolin (Figures 2 and 3) compositions 7 and 10 with 100/0 alumina/silica ratios performed the best.

Table V - Release Agent Ease of Application, Coating Quality, and Rating after 1 Firing

Comp. #	Alumina/Silica	Kaolin(%)	Ease of App.	Quality	Rating
1	100/0	0	poor	poor	4.5
2	50/50	0	poor	poor	4
3	0/100	0	fair	good	4
4	100/0	25	good	good	2
5	50/50	25	good	good	2
6	0/100	25	good	good	2
7	100/0	40	good	good	1.5
8	50/50	40	good	good	1.5
9	0/100	40	good	good	1.5
10	100/0	50	good	good	2
11	50/50	50	good	good	1.5
12	0/100	50	good	good	2
13	100/0	75	good	poor	--
14	50/50	75	good	poor	--
15	0/100	75	good	poor	--
16	100/0	100	good	poor	--
Mile Hi Ceramics kiln wash			good	good	1.5
Seattle Pottery Supply shelf paint			good	good	1.5
Hot Line Hi Fire shelf primer			good	poor	1.5
Thin Fire shelf paper			--	--	5

In Figures 4-6 the same release data as in Figures 1-3 are replotted for different alumina/silica ratios with curves representing the kaolin percentages. The data in these figures show that for all three alumina/silica ratios 40% kaolin results in the best release performance. Composition 7 (60% alumina hydrate and 40% kaolin) gave the best results of all nine compositions, but did eventually degrade to a rating of 3 after 14 firings.

The repeat firing results for the commercial compositions are plotted in Figure 7 with composition 7 included for comparison. The Hot Line Hi Fire release, which cracked after drying, gave the worst performance. The Seattle Pottery Supply release resulted in the best results, and had not degraded significantly even after 15 firings. Even with these excellent results a small amount of release did stick to the glass samples after each firing, and thus eventually the release layer will significantly degrade.

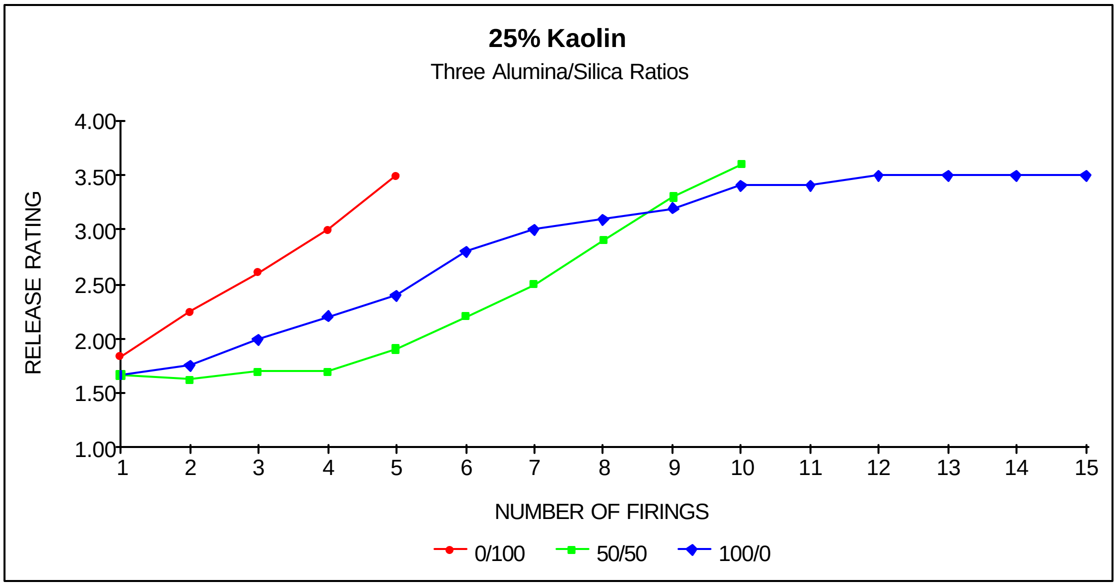

Figure 1 - Release rating plotted versus the number of firings for 25% kaolin compositions with three alumina/silica ratios (compositions 4, 5, and 6). The running averages of five data points are plotted.

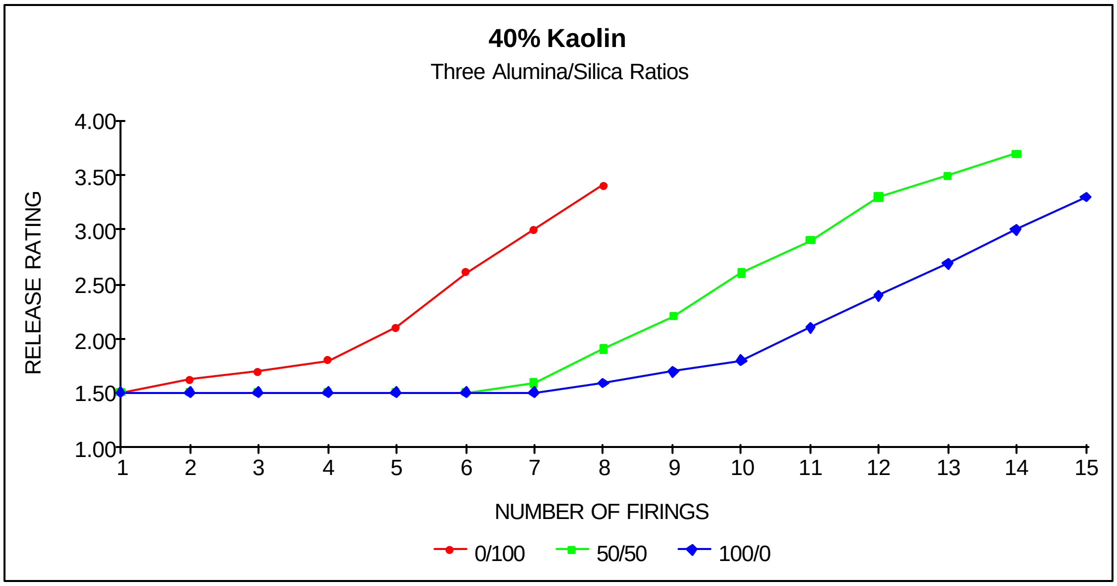

Figure 2 - Release rating plotted versus the number of firings for 40% kaolin compositions with three alumina/silica ratios (compositions 7, 8, and 9). The running averages of five data points are plotted.

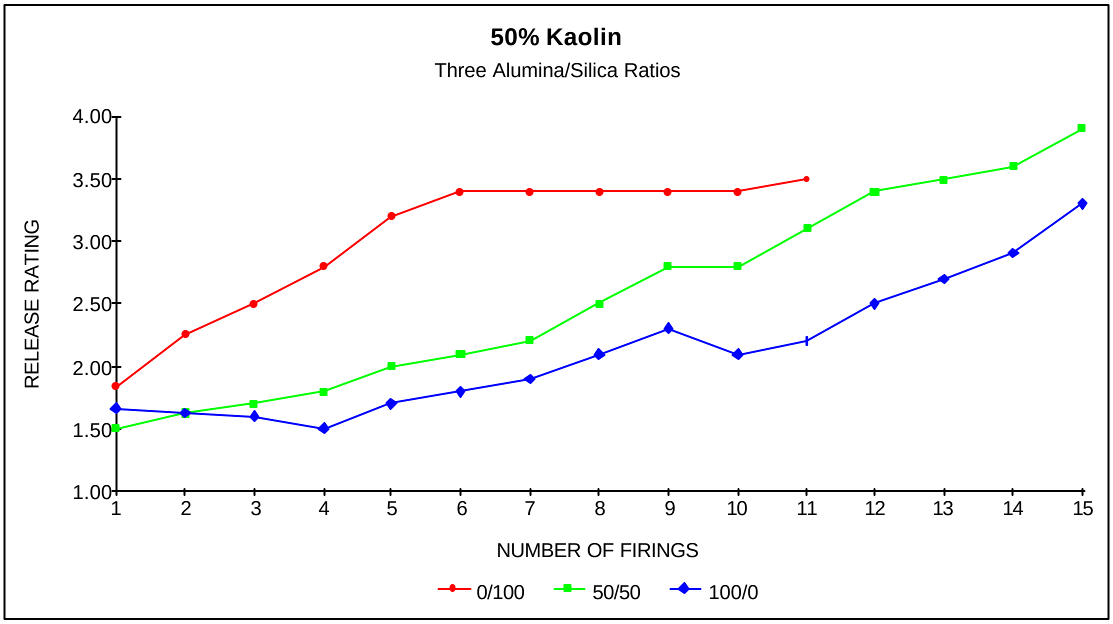

Figure 3 - Release rating plotted versus the number of firings for 50% kaolin compositions with three alumina/silica ratios (compositions 10, 11, 12). The running averages of five data points are plotted.

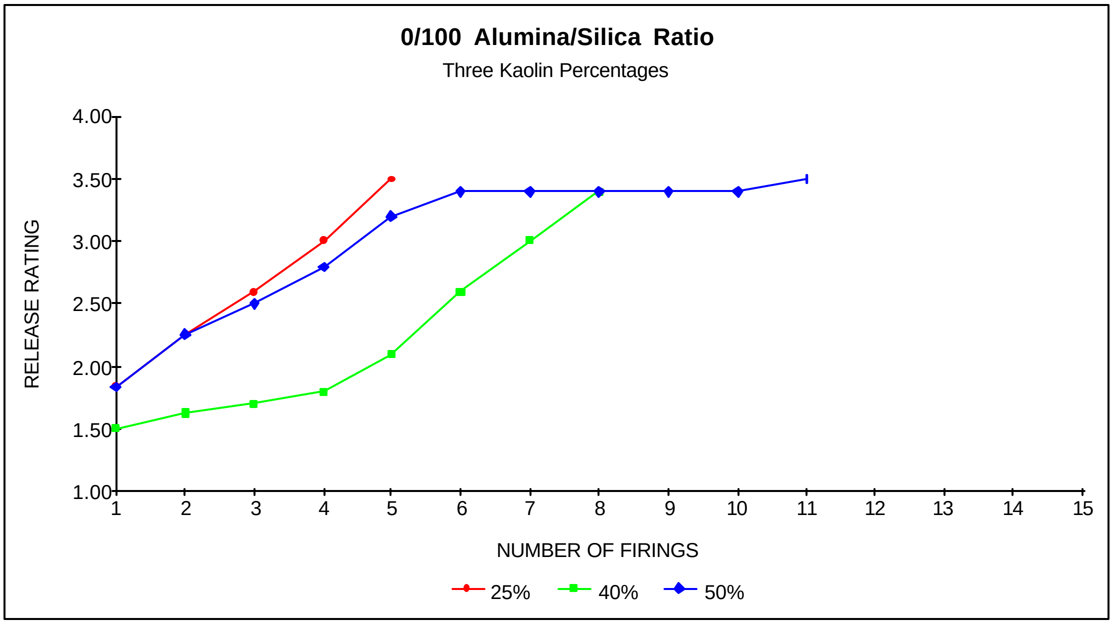

Figure 4 - Release rating plotted versus the number of firings for compositions with 0/100 alumina/silica ratio and different kaolin percentages (compositions 6, 9, and 12). The running averages of five data points are plotted.

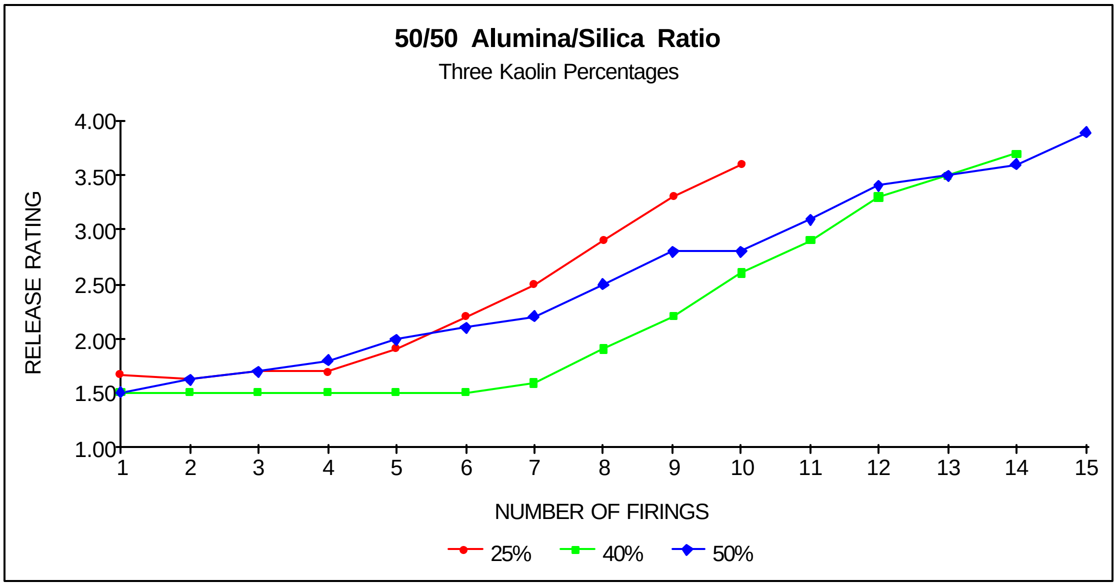

Figure 5 - Release rating plotted versus the number of firings for compositions with 50/50 alumina/silica ratio and different kaolin percentages (compositions 5, 8, and 11). The running averages of five data points are plotted.

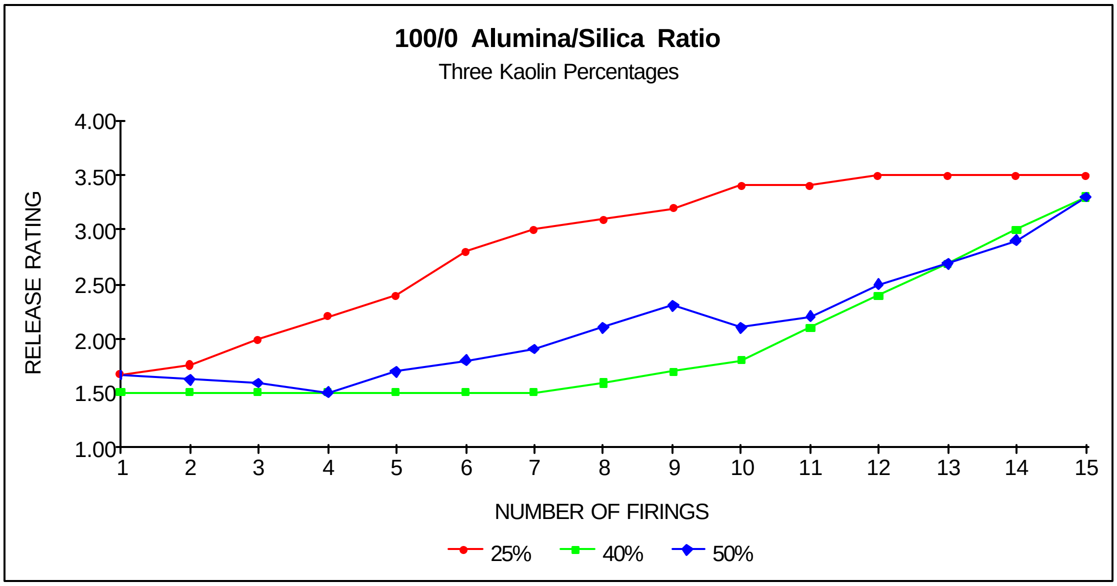

Figure 6 - Release rating plotted versus the number of firings for compositions with 100/0 alumina/silica ratio and different kaolin percentages (compositions 4, 7, and 10). The running averages of five data points are plotted.

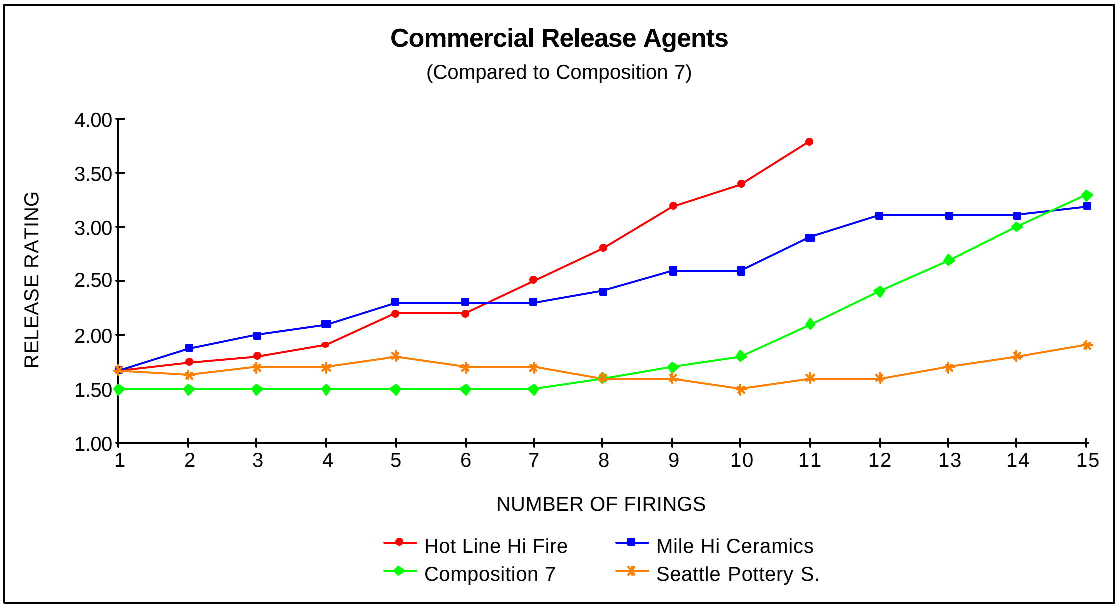

Figure 7 - Release rating plotted versus the number of firings for commercial release agents along with composition 7 (60% alumina hydrate and 40% kaolin). The running averages of five data points are plotted.

A series of studies were also conducted where the release agents were prefired without glass before initial testing. The results of this work in some cases indicated that prefiring slightly improved the release performance, but in other cases the performance was degraded. Based on these results, prefiring does not appear to be justified for releases based on the alumina-silica-kaolin system.

4.3 Crystallization Results

The TriVitro glass and bulk pieces of clear, green, and amber container glass were fired to a series of temperatures and hold times. The objectives of this work were to determine if the TriVitro glass could be fired to produce a smooth surface without a hazy appearance, and to further understand the crystallization behavior of soda-lime glass. The results of this study are summarized in Table VI.

The surfaces of the TriVitro glass samples were evaluated as being either rough or smooth, depending on the amount of glass flow that had occurred. The lowest temperatures which produced a smooth surface were 1500°F with a 1 hour hold, and 1540°F with a 5 minute hold. Firing at 1700°F for 5 minutes resulted in a roughened surface from extensive crystallization that occurred throughout the samples. All samples with smooth surfaces resulted in surface haze and crystallization. When the surfaces of the samples were rough, it was difficult to determine if surface haze was present, and thus a question mark was indicated in Table VI for these cases.

The last two columns in Table VI are the results for the presence of crystals as observed with an optical microscope. A question mark in the results indicates that crystals were not observed, but because these samples were not densified well with smooth surfaces, it was difficult to conclude definitely that crystals were not present. A Y? result indicates that a few crystals appeared to be present, but not enough to be definitive. Crystals were observed in both the bulk glass and crushed glass samples, but more clearly in the bulk samples. The clear glass appeared to produce more clusters of crystals, compared to the green and brown glass which tended to crystallize long acicular crystals. The crystals could often be seen to originate at defects and particles on the surface of the glass.

The results demonstrate that crystallization occurs as low as 1340°F and possibly 1300°F, with a 10 hr hold. Reducing the hold time decreased the crystallization, but in all cases where a smooth surface was produced crystallization and a surface haze also occurred. These results indicate that for the particular glass and processing conditions used, some degree of crystallization will occur when the glass flow is enough to produce a smooth surface.

Figure 8 shows x-ray diffraction patterns for the TriVitro glass fired to 1600 and 1700°F with 5 minute hold times. The lower curve for the 1600°F sample shows a broad amorphous peak centered about 30 degrees with the small fluctuations due to background noise. X-ray diffraction analysis software did not identify any crystalline peaks for this sample. However, a peak near 48 degrees appears to present. In either case, very little crystallization occurred in the 1600°F sample. X-ray diffraction can only detect crystallinity down to about one percent, and thus the surface haze that occurs only results in a small amount of crystallization.

The upper curve in Figure 8 for the 1700°F sample shows a series of crystalline peaks, along with a broad amorphous peak. The amorphous peak indicates that a large amount of residual glass still remains. The angles and d-spacings of the crystalline peaks as determined from analysis software are listed in Table VII. The major peaks present correspond to devitrite (Na_2O-$3CaO$-$6SiO_2$), with other minor phases also present.

Table VI - Summary of Crystallization Results

Firing Conditions	Smooth (S) or Rough (R) Surface	Haze on TriVitro Samples	Crystals on TriVitro Samples	Crystals on Bulk Glass Samples
1300°F-10hrs	R	?	?	Y?
1340°F-10hrs	R	?	Y?	Y
1360°F-10hrs	R	Y?	Y	Y
1400°F-5mins	R	?	?	?
1400°F-1hr	R	?	Y?	?
1400°F-10hrs	R	Y	Y	Y
1500°F-5mins	R	?	Y?	Y
1500°F-1hr	S	Y	Y	Y
1540°F-5mins	S	Y	Y	Y
1580°F-5mins	S	Y	Y	Y
1600°F-5mins	S	Y	Y	Y
1700°F-5mins	R	Y	Y	Y

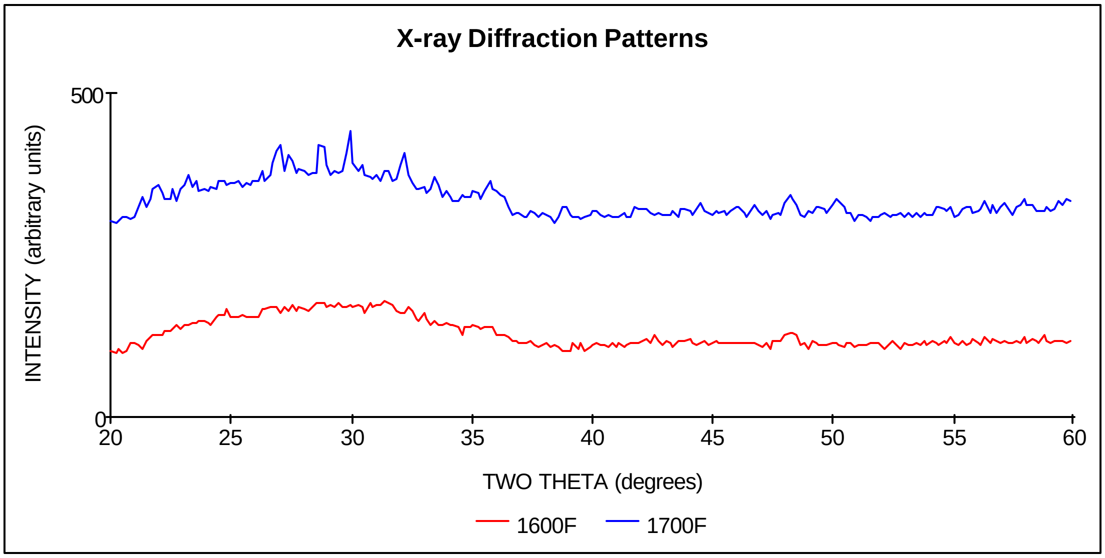

Figure 8 - X-ray diffraction patterns of TriVitro glass fired to 1600 and 1700F with 5 minute hold times.

Table VII - Crystalline X-ray Diffraction Peaks
(Fired at 1700° F with 5 min. Hold)

2 Theta	d-spacing	2 Theta	d-spacing
8.96	9.875	29.95	2.984
18.69	4.748	32.19	2.781
21.28	4.176	33.53	2.673
21.93	4.053	48.20	1.888
23.26	3.824	48.31	1.884
27.02	3.300	54.92	1.672
27.48	3.246	56.42	1.631
28.76	3.104		

5.0 SUMMARY AND CONCLUSIONS

The major results are summarized in this section divided into the release agent and crystallization studies.

Release Agents

- A semi-quantitative rating system was developed to compare the sticking behavior of different release agent compositions.
- Release agents consisting of only alumina hydrate, silica, or a 50/50 alumina/silica mixture did not hold together in a release layer well, and resulted in poor sticking results.
- Kaolin was needed to help disperse the initial slurry, and to bond the release layer together after drying and after firing.
- High amounts of kaolin (75 and 100%) resulted in cracking of the release layer after drying, and thus are not acceptable.
- Kaolin amounts of 25, 40, and 50% with alumina hydrate, silica, or a 50/50 mixture resulted in good release agent layers.
- Silica contributes to good release behavior for short firings, but not for repeat firings. This correlates with low surface tension, but relatively high diffusion.
- Prefiring the release in some cases slightly improved performance and in other cases degraded it. Thus prefiring does not appear to justify the extra step required.
- Alumina hydrate additions result in better repeat firing performance compared to silica additions.
- Of the compositions investigated in the alumina-silica-kaolin system 40% alumina hydrate and 60% kaolin gave the best repeat firing results.
- The Seattle Pottery Supply shelf paint resulted in the best overall results, and was still acceptable after 15 firings.
- At least a small amount of sticking occurred for all compositions and firings studied.

Crystallization

- A smooth surface occurred between firing at 1500°F for 5 min (rough surface) and 1540F for 5 min (smooth surface). Firing at 1500°F with a one hour hold resulted in a smooth surface, but 1400F for one hour resulted in a rough surface.
- Crystals were observed in an optical microscope at 40-400x in both the bulk glass and crushed glass samples, but more clearly in the bulk samples.
- The clear glass appeared to produce more clusters of crystals, compared to the green and amber glass which tended to crystallize long acicular crystals. The crystals could usually be identified as originating at defects and particles on the surface of the glass.
- Crystallization was observed after firing as low as 1340°F with a 10 hour hold; 1400°F with a one hour hold; and 1500°F with a five minute hold.
- All samples with enough glass flow to have an acceptably smooth surface also developed surface crystallization haze. Firing conditions to produce a smooth surface without surface crystallization does not appear to be possible with the system investigated.
- X-ray diffraction of a sample fired to 1600°F for 5 minutes indicated that the sample was x-ray amorphous (or only slightly crystallized), while firing to 1700°F crystallized the sample substantially, but still contained a large amount of residual glass.
- Devitrite appears to be the main crystalline phase after firing at 1700°F, but other minor crystalline phases were also present.

Conclusions and Recommendations for Future Work

Sintering of crushed soda-lime glass without sticking and crystallization problems is technically very challenging, because of the conflicting effects of a reduction in glass viscosity. Glass flow is required to fuse and sinter the particles together. The amount of viscosity reduction and flow that is needed increases with greater particle size and less efficient particle packing. Glass flow also has the negative effects of promoting sticking and crystallization. So the processing challenge involves producing enough glass flow to sinter the particles, but not enough to cause sticking and crystallization problems. With the particular glass and release agents used in this project, it does not appear possible to completely separate the densification process from the sticking and crystallization problems. A balance is required between the required degree of densification and the amount of sticking and crystallization that can be tolerated.

With future work, the glass and/or processing conditions can probably be modified to improve and possibly eliminate the sticking and crystallization problems. The variables that will have the most influence on producing the desired processing window are:

- Modifying the glass composition, and/or surface chemistry;
- Optimizing the glass particle size distribution, and particle packing
- Improving the release agents (possibly with some type of non-oxide ceramic, such as a nitride or carbide); and
- Including additives, such as fluxes or different glass compositions.

Additional research is needed to improve the understanding of the affects of glass composition (container vs. plate glass; clear vs. green vs. amber types) and surface chemistry on the densification, crystallization, and sticking behavior. Another area on future research could be to develop post-fire treatments to eliminate surface crystallization or stuck release.

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