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LEAD INDUSTRIES ASSOCIATION

60 EAST 42ND STREET
NEW YORK 17, N. Y.

December 13, 1957

SUBJECT: SUPPLEMENT TO "LEAD IN THE CERAMIC INDUSTRIES"

To Members of the Lead Industries Association:

Enclosed is the first supplement to our technical data book, "Lead in the Ceramic Industries," issued in December, 1956.

This is being mailed to all of the 5,000 people connected with the ceramic industries who have already received the book and will also be included with future copies of the book sent out in answer to requests for it. It will be followed by other supplements from time to time, some of which are already in preparation.

Very truly yours,

Robt L Ziegfeld

Secretary.

ENAMELS FOR APPLICATION TO GLASS*

Comparatively little has been published on the properties of glass enamels in spite of their wide use on many products, e.g., multiple trip beverage bottles, cosmetic containers, mixing bowls, casseroles, tumblers, lighting goods, structural glass, gift glassware, among others.

In the development of glass enamels, there are four properties of primary concern. These are stability of composition, chemical durability, coefficient of expansion, and melting temperature. While these properties are discussed more fully later in terms of specific compositions, the important considerations are outlined briefly below.

Stability of Composition—First the composition of the flux must be such that it will not devitrify under normal firing conditions, and second, it must not be sufficiently chemically reactive that compounds will be formed which adversely affect the color.

Chemical Durability—There is an increasing demand for enamels which have an extremely high resistance to acids and/or alkalies.

Enamels which come in contact with food must resist various acids and sulfides and concurrently resist the alkali detergents as used in automatic dishwashers. For tumbler decoration there is still some demand for soft, non-resistant colors, but as the use of mechanical dishwashers increases, this type enamel is giving way to those having greater detergent resistance. Multi-trip beverage bottle enamels are subjected to repeated washings in strong, hot detergent solutions. More recently there has been also a demand for ACL (applied color label) colors, which will withstand hot acids, particularly hydrochloric, since bottlers have found this acid to be very suitable for removing iron stains resulting from the metal closures. High acid-resistant colors serve best in the field of structural glass where colors are subject to attack by weather.

Coefficient of Expansion—The problem concerns attaining sufficiently low thermal expansion enamels to produce a satisfactory "fit." As a general practice it can be stated that an enamel, to have a good fit on the glass on which it is applied, should have a linear coefficient of expansion about three points lower than the expansion of the glass. For example, if a glass has a coefficient of 81×10^{-7}, then the enamel should have a coefficient of 78×10^{-7} or less. There is little chance of having too low a coefficient of the enamel, which could cause checking or weakening of the glass structure.

As the coefficient of expansion of the enamel is increased, the strength falls off rapidly. There is a noticeable weakening of the glass even when the coefficients of glass and enamel are similar. When the expansion of the enamel is ten points higher than the glass, spontaneous crazing will occur and frequently breakage of the glass. The heavier the enamel is applied, the greater will be the stress.

Melting Temperature—Since all enamels are applied to articles of pre-formed glass, it is essential that the enamel has a melting temperature far enough below the softening point of the glass that the enamel can be fired to a good gloss without causing deformation of the glass.

If other considerations such as stability of composition, chemical durability, and coefficient of expansion need not be considered, then the proper melting temperature would in itself be a very easy goal to achieve. However, to produce an enamel of sufficiently low expansion, with good chemical durability, and a melting temperature sufficiently low that it can be fired on articles of glass without any warpage or distortion presents a difficult problem.

Typical Compositions of Enamels

Table 6-2 gives the compositions of ten typical compositions ranging from the very lowest melting, non-resistant type to the higher melting varieties with excellent chemical durability. These compositions will serve to discuss more fully the considerations involved in their design.

ACL (applied color label) colors on these new Pyrex brand bowl sets must have high resistance to acids and/or alkalies

Courtesy, Corning Glass Works

* Ray Andrews, Manager, Glass Colors Division, B. F. Drakenfeld & Company, Incorporated, Washington, Pa.

Flux No. 1—Compositions such as this, which are extremely low melting due to their high lead content, tend to devitrify or crystallize if subjected to a high temperature for a prolonged period. When a flux devitrifies, it loses its glossy surface and a large increase in expansion occurs. One flux, having a coefficient of expansion of 75 x 10^{-7} increased to 140 x 10^{-7} after devitrification. In the event devitrification occurs in this type composition it can be corrected by either reducing the lead or increasing the silica content. As will be noted in Table 6-2 this is the lowest melting composition and attempts to attain lower melting have resulted in fluxes which are so unstable they devitrify during a normal firing cycle. Flux No. 1 will dissolve completely in about ten minutes in a solution of 5 percent acetic acid. Its alkali resistance is extremely poor.

Flux No. 2—The reduction in lead and increase in silica content increases the firing temperature and decreases the coefficient of expansion. However, there is only a slight improvement in chemical durability. Fluxes of this type still find some application where low firing temperature is essential and chemical durability is not an important factor.

Flux No. 3—The lead is further reduced and the silica and boric oxide contents increased resulting in increased melting temperature and lower expansion. However, this composition still has very poor chemical durability.

Flux No. 4—This composition represents one of the early attempts to produce a lead containing flux which would have improved chemical durability. A composition of this type is still quite soluble in dilute acids and is subject to attack by various alkali detergents. Perhaps the outstanding characteristic of a composition of this type is its low coefficient of expansion.

Cadmium oxide, which is a good fluxing agent and functions in this respect similarly to lead oxide, is used in lead containing enamels for the purpose of stabilizing cadmium sulpho-selenide red pigments. When this pigment is introduced in a lead flux not containing cadmium oxide, the mixture will fire black.

In 1934, a demand arose in the glass industry for fluxes which would have good chemical durability for use on both tableware and beverage containers. As a result of this demand, work was started to develop fluxes of good chemical durability.

Flux No. 5—This composition is an excellent example of the high fluxing power of sodium oxide. In comparing this with flux No. 4 the melting temperature was increased only twenty degrees in spite of the substantial reduction in boric oxide and increase in silica contents. Fluxes of this type have fairly good alkali resistance. When tested in accordance with the Bureau of Standards recommended test, this flux showed a lead solubility of about 500 parts per million.

Flux No. 6—As development work continued it was found that the introduction of titania into lead fluxes greatly increased the acid resistance. *Fluxes No. 5 and 6* are quite similar except that 4 percent titanium dioxide has been added and the alkali has been increased in order to accommodate this addition of a more refractory material with no increase in melting temperature. The lead solubility of the flux has been reduced from 500 parts per million to only 40 parts per million. A recommended procedure incorporating the Bureau of Standards test is included elsewhere in this section.

Flux No. 7—This composition employed lithia in combination with sodium oxide as secondary fluxes. Because there are very few glasses having so high a coefficient of expansion, this type flux would have a

TABLE 6-2

Typical Compositions of Glass Fluxes

(% Oxide Composition)

	1	2	3	4	5	6	7	8	9	10
PbO	81.8	78.8	66.6	60.4	59.5	55.5	45.5	52.1	49.4	48.6
B_2O_3	10.6	9.6	18.6	5.2	3.0	3.0	2.2	2.0	3.3	6.9
SiO_2	7.6	11.6	14.8	21.4	32.2	29.6	36.3	31.7	36.4	28.0
Al_2O_3	-	-	-	3.0	-	-	-	-	-	-
CaO	-	-	-	7.8	4.0	3.3	4.3	3.8	3.3	3.6
Na_2O	-	-	-	-	1.5	4.4	4.8	3.3	4.0	3.3
TiO_2	-	-	-	-	-	4.0	4.9	4.3	3.6	3.4
Li_2O	-	-	-	-	-	-	2.0	1.8	1.5	-
ZrO_2	-	-	-	-	-	-	-	-	6.7	6.7
Na_2SiF_6	-	-	-	-	-	-	-	-	-	3.6
Firing Temperature (°F.)	830	950	1050	1100	1120	1120	1100	1080	1100	1120
Firing Temperature (°C.)	454	510	567	593	604	604	593	567	593	604
Coefficient of Expansion (x10^{-7})	104	85	76	73	78	89	97	90	98	85
Lead Solubility (parts per million)	∞	∞	∞	∞	500	40	2	60	100	100
Alkali Resistance	-	-	-	Fair	Good	Good	Good	Good	Exc.	Exc.

Note: ∞ indicates complete solubility.

The leaded glass enamels used for decorating lighting fixtures have a sufficiently low thermal expansion to produce a satisfactory "fit."

limited field of application. However, this flux has very low lead solubility and possesses excellent weathering characteristics as needed in the field of structural glass.

Flux No. 8—This composition provides for a decrease in melting temperature of about 50 F. resulting essentially from the increase in the lead oxide and decrease in silica contents (as compared with the previous flux). There is almost no change in the coefficient of expansion but there is a marked increase in lead solubility.

This type composition offers the possibility of devitrification in another fashion than heretofore discussed. If overfired the lead oxide may combine with titania to form yellow lead titania and adversely affect the color. If heating is continued for a prolonged period, sufficient devitrification may occur and result in loss of gloss and greatly increased coefficient of expansion. The condition can be improved by reducing the alkali or lead oxide and increasing the silica contents.

Flux No. 9—With the development of compositions similar to No. 7 the problem of acid resistance became less important and attention was turned towards attaining greater alkali resistance. It was found that outstanding improvements in resistance to alkali detergents could be achieved by additions of *zirconia*. In respect to chemical durability *Fluxes No. 9 and 10* meet the requirements of the bottle trade very satisfactorily. However, the coefficient of expansion of No. 9 is high.

Flux No. 10—This composition provided for a reduction in coefficient of thermal expansion. The alkali fluorides are valuable as fluxing agents and are also very beneficial in the development of bright reds. This composition provides for excellent acid resistance and has proven to give good service in the field.

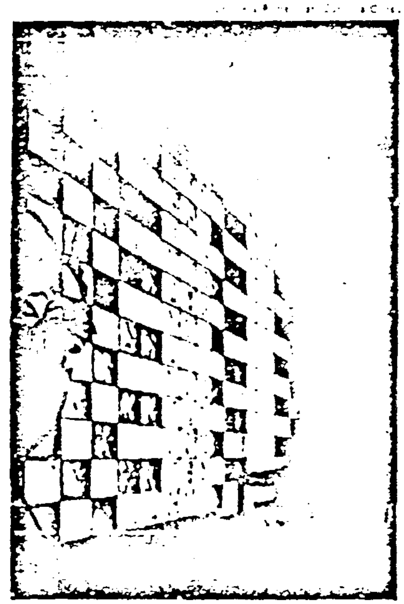
Summary

Enamels for glass can be roughly divided into two groups; the low-resistant or non-resistant enamels (*Fluxes No. 1-4*) and the resistant type enamels (*Fluxes No 5-10*).

Lead oxide is the primary flux in glass enamels. Boric oxide is only moderately active as a fluxing agent; however, it is extremely valuable for the reduction of coefficient of expansion. It lowers chemical durability very rapidly as it is increased.

Cadmium oxide is valuable as a fluxing agent and essential as a stabilizer for the production of bright reds and cadmium yellows.

Both sodium and lithium oxides are valuable as fluxing agents providing for the addition of larger amounts of silica and for the introduction of titania and zirconia. The alkali oxides, however, raise the



Available in four colors, glass building blocks have a leaded glass enamel finish on one side that is translucent and permanent.

coefficient of expansion very rapidly and reduce chemical durability.

The alkali fluorides are good fluxes and aid in the development of bright reds. However, they increase expansion and reduce durability.

Silica contributes materially to chemical durability, especially acid resistance. It lowers the coefficient of expansion and increases melting temperature.

Titania is valuable for the improvement of acid resistance.

Zirconia is essential to the production of enamels having good alkali resistance.

Lead Solubility Test

Materials Required

1. 50 grams glass color ground in alcohol and water.
2. Glass tea cups or nappies of about 150 cc. capacity.
3. Standard lead acetate solution.
4. Heinz's distilled white vinegar.
5. Several 250 cc. Pyrex beakers.
6. Hydrogen sulphide.

Procedure

Fifty grams of the color being tested is milled in a ball mill with about 20 cc. of a mixture of 3 parts water and 1 part alcohol for a period of fifteen to twenty minutes. The color is transferred to a spray bottle and two or three drops of 40 percent solution of magnesium sulphate is added. This will improve the spraying qualities of the color considerably. After they are sprayed, the pieces of glass are placed in a kiln or furnace at about 700-800 F. and the temperature carried up to 1100 or 1150 F. depending on the exact type of color being fired. They are held at this temperature for a period of ten to fifteen minutes and allowed to cool in the furnace. The color is then ready for testing.

One hundred cc. of Heinz's distilled white vinegar is placed in a 250 cc. beaker and brought to a boil. This is poured into the cup or nappy being tested and allowed to cool for exactly one-half hour. The vinegar is then poured back into the original beaker without policing or in any way disturbing the surface of the color. Hydrogen Sulphide is then bubbled through the lead-containing vinegar for a period of three and one-half minutes. The color developed is then compared with the color of *freshly* prepared standards.

Standards

A standard solution of lead acetate is prepared by dissolving 108 mgm. of lead acetate CP Crystals ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$) in Heinz's white distilled vinegar and then made up to exactly 300 cc. One cc. of this solution is diluted to 100 cc. with vinegar and placed in a 250 cc. beaker. This is equivalent to 2 parts of PbO per million parts of vinegar. Two cc. of lead acetate solution diluted to 100 cc. with vinegar is equivalent to 4 parts PbO per million, and so on.

Through this standard solution is bubbled hydrogen sulphide for a period of three and one-half minutes. The color of this standard solution is then compared with the color of the vinegar from the test. If the lead solubility of the enamel being tested exceeds 20 parts per million, the color of the vinegar after bubbling the hydrogen sulphide through it will be so dark as to make comparison inaccurate or impossible. In this case, it is necessary to take an aliquot and dilute it to a suitable concentration. We have found that for most cases, a 25 cc. aliquot diluted to 100 cc. with vinegar works quite well.

In running lead solubility tests, it is advisable to run all of them in duplicate. If the glass being used has an expansion of more than 90×10^{-7}/°C, it is advisable to warm the cups or nappies in water before pouring the vinegar into them. This will avoid breakage. Color comparison should be made in diffused daylight on a white table top or other white material.