

## A CLASSIFICATION OF ENAMELS FOR SHEET STEEL\*

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An inspection of commercial formulas for sheet steel enamels shows a considerable variation in the chemical composition; in certain instances even in the case of enamels used for the same type of ware. In spite of these permissible variations a study of a large number of commercial formulas shows that there are certain typical classes into which these various compositions can be grouped.

Sheet steel enamels may be classified generally into two rather distinct groups, that is the gray or so called granite ware enamels and the three-coat enamels. In this first group we have a single coat of enamel applied to the metal, and mottled by the formation of rust spots on the metal. This ware is given a single firing when it is finished and ready for the trade. Enamels typical of this group are shown in table 1.

The melted compositions are shown on the same table, it being assumed in computing these that such materials as feldspar, fluorspar and bone ash lose no weight in smelting. Gray enamel A is typical of some of the earlier types of gray ware enamel containing a comparatively high content of quartz in addition to feldspar as a refractory. It contains considerable opacifying agents in the form of fluorspar, bone ash and antimony oxide.

TABLE 1—GRAY WARE ENAMELS  
Raw Batch Composition of Frits

	A	B	C
Feldspar.....	30.0	40.0	48
Borax.....	28.5	30.5	40
Quartz.....	19.0	10.0	...
Soda ash.....	8.0	6.5	3.0
Sodium nitrate.....	4.0	5.5	4.0
Fluorspar.....	3.0	1.5	...
Bone ash.....	5.0	4.5	3.5
Antimony oxide.....	2.5	1.5	1.5
Total.....	100.0	100.0	100.0

*Mill Batch:* Frit 100.0, clay 6.0, magnesium carbonate 0.25, water 50.0.

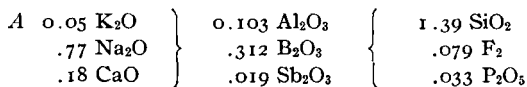
\* Read at the meeting of the Society at the Chemical Exposition, New York City, Sept. 24, 1920.

Percentage Composition of Melted Frits

	A	B	C
Feldspar.....	37.2	50.3	62.05
Quartz.....	23.5	12.6	..
B <sub>2</sub> O <sub>3</sub> .....	12.8	14.1	18.9
Na <sub>2</sub> O.....	13.4	13.5	12.6
Fluorspar.....	3.7	1.9	..
Bone ash.....	6.3	5.7	4.5
Antimony oxide.....	3.1	1.9	1.95
Total.....	100.0	100.0	100.0

TABLE 2—GRAY WARE ENAMELS

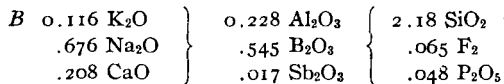
## Empirical Formulas



1.00

$$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 4.46$$

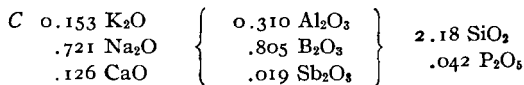
$$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 13.5$$



1.000

$$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 4.0$$

$$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 9.56$$



1.000

$$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 2.7$$

$$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 7.03$$

Gray ware enamel B is a type showing the tendency to reduce the amount of quartz and replace it with feldspar. There is apparent a desire to reduce the amount of antimony oxide and of fluorspar, and we note a slight increase in the content of boric

oxide probably to retain a fusing temperature similar to that of enamel A.

Gray enamel C is a type much in use at the present time. Quartz has been eliminated entirely and has been replaced by feldspar which remains as the sole refractory. Fluorspar has been eliminated and the boric acid increased to care for the decrease of other fluxes. It is to be noted in the three types that the content of sodium oxide remains fairly constant, and this is undoubtedly due to the fact that higher amounts of sodium oxide give difficulties from blistering and boiling. The next change in this class of enamels will probably be in the elimination of antimony oxide and its replacement by some opacifying agent to which there is not attached the prejudice now associated with antimony.

The usual mill additions to the gray ware frits consist of about six per cent of some high grade ball clay, one-fourth of one per cent of magnesium carbonate and about one-fourth of one per cent of some electrolyte, such as magnesium sulphate or cobalt and nickel sulphates. These sulphates play a part in tempering the enamel to such a viscosity that it may be properly applied to the steel and also promote rusting of the metal, which gives rise to the mottled granite appearance. Certain plants make use of small amounts of metallic oxides to produce various shades of gray, but the amounts added are usually so small that they do not play any material part in the behavior of the enamel. These oxides are added to the raw enamel batch previous to smelting and may consist of 0.01 to 0.02 per cent of cobalt oxide and 0.2 to 0.3 per cent of nickel, manganese or iron oxides.

The empirical formulas for these three gray ware enamels have been calculated and are shown in table 2. It has been assumed for these and subsequent calculations that all the materials entering into the enamels have approached the theoretical compositions, which is true of most enamel ingredients except that of feldspar. For this we have assumed the composition of an average Connecticut feldspar with the following percentage composition: 71  $\text{SiO}_2$ , 17  $\text{Al}_2\text{O}_3$ , 8  $\text{K}_2\text{O}$  and 4  $\text{Na}_2\text{O}$ . A study of these empirical formulas shows a slight decrease in the refractoriness, due principally to a decrease in the silica-boric oxide ratio.

TABLE 3—GROUND COATS

## Raw Batch Composition of Frits

	A	B	C
Borax.....	30.0	30.0	39.5
Feldspar.....	22.0	27.0	20.5
Quartz.....	29.0	20.5	22.5
Soda ash.....	5.0	9.8	5.0
Soda nitre.....	4.6	5.0	4.7
Fluorspar.....	6.0	6.0	6.0
Cobalt oxide.....	0.4	0.5	0.4
Manganese oxide.....	2.0	1.2	1.0
Nickel oxide.....	1.0	...	0.4
Total.....	100.0	100.0	100.0

*Mill Batch:* Frit 100.0, clay 7.0, borax 1.5, water 50.

## Percentage Composition of Melted Frits

	A	B	C
Feldspar.....	27.2	34.3	26.9
Quartz.....	36.0	26.2	29.6
B <sub>2</sub> O <sub>3</sub> .....	13.6	14.0	18.9
Na <sub>2</sub> O.....	11.6	15.8	14.4
CaF <sub>2</sub> .....	7.4	7.6	7.9
CoO.....	0.5	0.63	0.5
MnO.....	2.47	1.5	1.3
NiO.....	1.23	..	0.5
Total.....	100.0	100.0	100.0

TABLE 4—GROUND COATS

## Empirical Formulas

A	0.5490 Na <sub>2</sub> O	$\left. \begin{array}{l} 0.1203 \text{ Al}_2\text{O}_3 \\ .5175 \text{ B}_2\text{O}_3 \end{array} \right\} \begin{array}{l} 2.445 \text{ SiO}_2 \\ .2530 \text{ F}_2 \end{array}$
	.0615 K <sub>2</sub> O	
	.2530 CaO	
	.0164 CoO	
	.0757 MnO	
	.0444 NiO	
	1.0000	
	$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 4.73$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 20.3$

B	0.6399 Na <sub>2</sub> O	}	0.1322 Al <sub>2</sub> O <sub>3</sub>	{	1.9200 SiO <sub>2</sub>
	.0673 K <sub>2</sub> O				
	.2260 CaO				
	.0182 CoO				
	.0486 MnO				
	1.0000				
	$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 4.16$				$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 14.5$
C	0.6222 Na <sub>2</sub> O	}	0.1120 Al <sub>2</sub> O <sub>3</sub>	{	2.008 SiO <sub>2</sub>
	.0558 K <sub>2</sub> O				
	.2502 CaO				
	.0162 CoO				
	.0374 MnO				
	.0182 NiO				
	1.0000				
	$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 3.0$				$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 17.9$

Three coat enameled ware, as its name indicates, is coated with three coats, a ground and two cover enamels. The following compositions given in table 3 are typical of ground coats in American practice. They may be grouped according to the type of ware to which they are applied as well as upon their refractoriness.

Ground A is a refractory enamel because of its high content of quartz and low amount of fluxes and for that reason is not adapted to lighter gauge shaped ware or to flat ware, such as signs and stove work, which would tend to buckle in the comparatively high temperature required for its fusion. It is used with success on heavy gauges of shaped ware such as enameled pipe, pails and containers. Because of its high content of metallic oxides, it is a tough durable enamel giving excellent service on ware subjected to hard service.

Ground B is one in use for flat ware such as stove work, table tops and two or three color signs and for medium gauge shaped ware. It is a high sodium oxide enamel with a medium content of refractories and is fired at a medium temperature.

Ground C is a type which has been used on light gauge drawn and spun ware. Because of its high boric oxide content it is not

desirable for the manufacture of flat ware where there is an opportunity for free expansion and contraction of the metal. It has a low fusion temperature, because of its low content of refractories and increased content of fluxes.

The empirical formulas are shown in table 4 and the silica-boric oxide ratios show the increase in boric oxide content.

### Cover Enamels

Cover enamels for ordinary three coat ware may be classified in two general groups, as white and colored enamels. The main distinction between these groups is in the content of opacifying agents. The compositions under white enamels shown in table 5 are typical of those which have been used with success and indicate a gradual evolution from the original.

White Enamel A is similar to German enamels in which the feldspar is low and the antimony oxide high. Very often this type is made up with small additions of clay in the raw batch, which would tend to overcome the effect of small amounts of feldspar.

White Enamel B shows an increase in the feldspar content and a decrease in the antimony oxide with the same content of fluorspar and cryolite. The increase in feldspar is compensated for by a decrease in the quartz content.

White Enamel C is a type which is used considerably where a very opaque enamel is demanded. It is the most refractory enamel of the three, carrying increased refractories and a smaller content of borax. This decrease in borax is taken care of by the replacement of fluorspar by cryolite, which exerts a greater fluxing action. Empirical formulas for the white enamels are shown on table 6.

The usual mill additions for these types consist of six per cent of a high grade ball clay or some plastic kaolin, seven per cent of tin oxide and 0.5 per cent of magnesium carbonate which aids in the flotation of the prepared enamels.

### Colored Enamels

Colored enamels differ from white enamels in that they are usually low in opacifying agents and hence have taken the name of glass or glass frit. Two types are shown in table 7.

Glass A is one which works well for dark colors because of its small content of opacifying agents. Glass B with its high content of opacifiers serves well for light colored enamels as it tends to mask the dark underlying ground coat. A comparison of glasses A and B shows that the main difference is in the decrease of feldspar and increase of fluorspar and cryolite.

Blue and black enamels are made by adding metallic oxides to the raw batch previous to smelting, while the others are produced by milling some oxide or color stain with the frit in the mills. This is done simply because of the intense coloring effect of cobalt which requires the intimate mixture with the other ingredients that is obtained on smelting.

TABLE 5—WHITE COVER ENAMELS  
Raw Batch Composition of Frits

	A	B	C
Borax.....	28.0	27.0	21.0
Feldspar.....	25.0	31.0	31.0
Quartz.....	19.0	17.0	22.0
Soda ash.....	3.5	3.5	3.5
Sodium nitrate.....	3.5	3.5	3.5
Fluorspar.....	5.0	5.0	...
Cryolite.....	12.0	12.0	17.0
Antimony oxide.....	4.0	1.0	2.0
Total.....	100.0	100.0	100.0

*Mill Batch:* Frit 100.0, clay 6.0, tin oxide 7.0, magnesium carbonate 0.5, water 60.0.

Percentages Composition of Melted Frits

	A	B	C
Feldspar.....	30.1	37.0	35.8
Quartz.....	23.0	20.5	25.5
B <sub>2</sub> O <sub>3</sub> .....	12.3	11.8	8.9
Na <sub>2</sub> O.....	9.4	9.2	7.8
CaF <sub>2</sub> .....	6.0	6.0	...
Cryolite.....	14.4	14.3	19.7
Antimony oxide.....	4.8	1.2	2.3
Total.....	100.0	100.0	100.0

TABLE 6—WHITE COVER ENAMELS

Empirical Formulas					
A	0.067 K <sub>2</sub> O	}	0.226 Al <sub>2</sub> O <sub>3</sub>	}	1.95 SiO <sub>2</sub>
	.730 Na <sub>2</sub> O		.458 B <sub>2</sub> O <sub>3</sub>		.741 F <sub>2</sub>
	.203 CaO		.044 Sb <sub>2</sub> O <sub>3</sub>		
	—				
	1.000				
	$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 4.27$		$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 8.64$		
B	0.084 K <sub>2</sub> O	}	0.252 Al <sub>2</sub> O <sub>3</sub>	}	2.03 SiO <sub>2</sub>
	.716 Na <sub>2</sub> O		.448 B <sub>2</sub> O <sub>3</sub>		.735 F <sub>2</sub>
	.200 CaO		.011 Sb <sub>2</sub> O <sub>3</sub>		
	—				
	1.000				
	$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 4.53$		$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 8.06$		
C	0.098 K <sub>2</sub> O	}	0.337 Al <sub>2</sub> O <sub>3</sub>	}	2.66 SiO <sub>2</sub>
	.902 Na <sub>2</sub> O		.398 B <sub>2</sub> O <sub>3</sub>		.880 F <sub>2</sub>
	—		.025 Sb <sub>2</sub> O <sub>3</sub>		
	1.000				
	$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 6.68$		$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 7.90$		

TABLE 7—GLASS FRITS FOR COLORED ENAMELS

Raw Batch Composition of Frits		
	A	B
Borax.....	29.0	29.0
Feldspar.....	24.0	14.0
Quartz.....	30.0	28.0
Soda ash.....	10.0	10.0
Sodium nitrate.....	3.0	5.0
Fluorspar.....	..	7.0
Cryolite.....	4.0	7.0
Total.....	100.0	100.0

*Mill Batch:* Frit 100.0, clay 6.0, magnesium carbonate 0.5, water 50.0, additions of necessary stains or oxides.



Percentage Composition of Melted Frits

	A	B
Feldspar.....	30.0	17.75
Quartz.....	37.4	35.25
B <sub>2</sub> O <sub>3</sub> .....	13.15	13.7
Na <sub>2</sub> O.....	14.45	15.7
Fluorspar.....	..	8.8
Cryolite.....	5.0	8.8
Total.....	100.0	100.0

TABLE 8—GLASS FRITS FOR COLORS

Empirical Formulas

$  \begin{array}{r}  A \quad 0.917 \text{ Na}_2\text{O} \\  \quad .083 \text{ K}_2\text{O} \\  \hline  1.000  \end{array}  \left. \vphantom{\begin{array}{r} 0.917 \\ .083 \\ 1.000 \end{array}} \right\}  $	$  \begin{array}{r}  0.202 \text{ Al}_2\text{O}_3 \\  .615 \text{ B}_2\text{O}_3  \end{array}  \left\{ \begin{array}{l} 3.17 \text{ SiO}_2 \\ .23 \text{ F}_2 \end{array} \right.  $
$  \frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 5.15  $	$  \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 15.7  $
$  \begin{array}{r}  B \quad 0.717 \text{ Na}_2\text{O} \\  \quad .033 \text{ K}_2\text{O} \\  \quad .250 \text{ CaO} \\  \hline  1.000  \end{array}  \left. \vphantom{\begin{array}{r} 0.717 \\ .033 \\ .250 \\ 1.000 \end{array}} \right\}  $	$  \begin{array}{r}  0.111 \text{ Al}_2\text{O}_3 \\  .421 \text{ B}_2\text{O}_3  \end{array}  \left\{ \begin{array}{l} 1.75 \text{ SiO}_2 \\ .532 \text{ F}_2 \end{array} \right.  $
$  \frac{\text{SiO}_2}{\text{B}_2\text{O}_3} = 4.17  $	$  \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 15.8  $

The following figures will give some idea of the methods of obtaining various colors:

*Blue:* Glass A plus 4 per cent black cobalt oxide and 2 per cent manganese dioxide in raw batch.

*Black:* Glass A plus 1.5 per cent cobalt oxide, 3.0 per cent manganese oxide, 1 per cent chromium oxide, 0.5 per cent copper oxide and 1.5 per cent iron oxide in raw batch.

The following colors may be produced by additions of oxides or stains to Glass A or B in the mill:

*Yellow:* 3 to 5 per cent cadmium sulphide.

*Green:* 3 to 5 per cent chromium oxide.

Other colors may be produced by the addition of from one to five per cent of stain, which may be procured on the market.

Since these stains can not be prepared successfully on a small scale in the individual plants, the various shades of colors can be best produced by the use of these prepared stains.

### Summary

In this paper have been given the compositions of typical enamels applied to sheet steel together with reasons for their use. It has not been intended to cover the field of possible composition but it has been the purpose of the writer to present proven compositions which yield the several kinds of commercial enamels and enable the makers of enamels to compare them with their own.

BUREAU OF STANDARDS  
WASHINGTON, D. C.

NOTICE.—*Further discussion of this subject is solicited. All communications should be sent to the Editor.*