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GROUND COAT ENAMEL FOR STAINLESS STEEL

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Refractory ceramic base coatings were formulated and developed for application to low-carbon steel. These coatings would protect this metal from oxidation, deterioration and avoid reduction of the cover-coat enamel by the stainless steel. Several of the coatings developed for iron were successfully applied to stainless steel. Indigenous raw materials such as quartz, feldspar and fluorspar which form the greater part of ground coat batch compositions have been used.

Key words: Enamel, Ground coat, Ceramic.

INTRODUCTION

Stainless steel has been used in almost all costly machinery and the various parts of air-craft engines all over the world. The use of stainless steel is desirable because this material retains a greater percentage of its initial strength and has longer life at elevated temperature than most metals. Efforts have been made to develop ground-coat enamel for stainless steel in order to increase the life of these parts of costly machinery and air-craft engine and to overcome replacement costs.

This study is limited to the consideration of cobalt-nickel bearing ground coat frits for stainless steel. These blue or cobalt ground coat frits fall within a narrow range of compositions and properties. They are given in Table 1, 2 and 3.

EXPERIMENTAL

Various compositions of ground coat enamels for stainless steel were formed (Table 1, 2 and 3) and applied either by dipping or spraying the test pieces which were already properly pickled. They were completely dried in an open atmosphere and subjected to firing operation in an electric furnace at 850^{o}-950^{o} for 3 to 4 minutes.

RESULTS AND DISCUSSION

The enamel glasses are really solutions [1] and, therefore, their properties are additive functions of the properties contributed by the constituent oxides and radicals.

One principle that seems to be fundamental in making a good ground coat for stainless steel is that when the ware goes into the furnace, the ground coat should contain a certain amount of raw materials. The presence of this can be secured by adding raw materials at the mill. The philosophy of the presence of this raw material seems to be that as the ware heats up, the raw material is gradually dissolved by the rest of the glass and the glass does not volatilize so readily. 6 % K.D. clay has been selected for use as mill addition in all the ground coat enamel compositions recorded in Table 1, 2 and 3. High content of clay (i.e., alumina) is avoided as it prevents the ground coat fluxing adhesively to the stainless steel and makes the surface uneven after firing. The chemical analysis of K.D. clay is given in Table 4.

Silica tends to increase the refractoriness and chemical resistance of an enamel. It has been used from 35.5 to 55.50 % in the ground enamel compositions from No. 1 to No. 21 (Table 1). Enamels containing high percentage of silica and low content of fluxes were extremely refractory, that is they were very viscous and difficult to smelt down. Silica ranging from 11.4 to 29.0 % was added to the enamel compositions from No. 1 to No. 17 in Table 2 and 30.5 to 48.5 % in enamel No. 1 to No. 10 in Table 3. After thorough investigations, it was found that compositions bearing 30.5 to 40.5 % silica were satisfactory. They yielded good adherence and better texture. Compositions No. 1,5,14,15 in Table 2 containing low content of silica and high content of fluxes developed good adherence to the steel but were easily scratched and chipped off by the slight impact.

A high feldspar content in the ground coat enamels is supposed to decrease the resistance to mechanical and thermal shock. It has been used upto 20 % in all the batch compositions of Table 1, 20-26 % in Table 3 and 18-32 % in Table 2.

Borax has been used in all the ground coat enamel compositions from 27.75-39.5 % in Table 2, 20-26 % in Table 3 and 9.50-29.5 % in Table 1. Enamels containing borax from 30-35 % melted excellently and dissolved the surface contamination on the stainless steel sheet. Enamels having borax from 9.5 to 15.5 % and SiO_2 50-60 % were

Table 1. Mill addition: 6 % K.D, clay was added as mill addition to each of the compositions.

Borax	Feldspar	Quartz	Soda ash	Red lead	Soda niter	Fluorspar	Cobalt oxide	Nickel oxide	Manganese dioxide	Total
29.50	20.00	35.50	5.50	5.00	4.50	3.00	0.25	1.25	0.50	100.00
28.50	20.00	36.50	5.50	4.50	4.50	3.00	0.25	1.25	0.50	100.00
27.50	20.00	37.50	5.50	4.50	4.50	3.00	0.25	1.25	0.50	100.00
26.50	20.00	38.50	5.50	3.50	4.50	3.00	0.25	1.25	0.50	100.00
25.50	20.00	39.50	5.50	3.00	4.50	3.00	0.25	1.25	0.50	100.00
24.50	20.00	40.50	5.50	2.50	4.50	3.00	0.25	1.25	0.50	100.00
23.50	20.00	41.50	5.50	2.00	4.50	3.00	0.25	1.25	0.50	100.00
22.50	20.00	42.50	5.50	1.50	4.50	3.00	0.25	1.25	0.50	100.00
21.50	20.00	43.50	5.50	1.00	4.50	3.00	0.25	1.25	0.50	100.00
20.50	20.00	44.50	5.50	0.00	4.40	3.00	0.25	1.25	0.50	100.00
19.50	20.00	45.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
18.50	20.00	46.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
17.50	20.00	47.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
16.50	20.00	48.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
15.50	20.00	49.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
14.50	20.00	50.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
13.50	20.00	51.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
12.50	20.00	52.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
11.50	20.00	53.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
10.50	20.00	54.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00
9.50	20.00	55.50	5.50	0.00	4.50	3.00	0.25	1.25	0.50	100.00

Table 2. 6 % K.D, clay was added as mill addition to each of the compositions.

Borax	Feldspar	Quartz	Soda ash	Sodaniter	Fluor spar	Barium carbonate	Sodium silico-fluoride	Cobalt oxide	Nickel oxide	Manganese oxide
36.00	32.00	15.00	7.00	–	5.0	–	–	0.5	0.3	1.5
35.00	18.00	29.00	5.50	5.0	5.0	–	–	0.5	0.5	1.5
35.00	20.00	18.00	5.50	5.0	5.0	9.0	–	0.5	0.5	1.5
35.00	20.00	22.00	6.50	5.0	9.0	–	–	0.5	0.5	1.5
37.10	31.00	11.04	5.09	3.8	9.0	–	–	0.5	0.4	0.9
32.00	30.00	20.00	7.00	4.0	5.0	–	–	0.5	–	1.5
30.00	22.00	29.00	5.00	4.6	6.0	–	–	0.4	1.0	2.0
30.00	27.00	20.05	0.08	5.0	6.0	–	–	0.4	1.0	2.0
39.50	20.05	22.00	5.00	4.7	6.0	–	–	0.4	0.0	1.0
35.00	21.00	21.00	6.00	4.5	10.0	–	–	0.5	0.5	1.5
35.00	21.00	28.00	4.05	4.0	5.0	–	–	0.5	0.5	1.5
32.05	29.05	23.00	4.00	3.0	5.5	–	–	0.5	0.5	1.5
27.75	28.75	21.00	5.05	4.0	6.2	4.3	–	0.5	0.5	1.5
32.05	28.00	16.00	7.00	4.5	5.0	5.0	–	0.5	0.5	1.5
32.00	30.00	15.00	8.00	5.0	4.00	–	3.5	0.5	0.5	1.5

Table 3. 6 % K.D clay was added as mill addition to each of the compositions.

Sr. No. Materials	1	2	3	4	5	6	7	8	9	10
Feldspar	8.00	10.00	12.00	14.00	16.00	18.00	20.00	22.00	24.00	26.00
Borax	20.00	20.00	20.00	22.00	22.00	22.00	24.00	24.00	24.00	26.00
Quartz	48.5	46.5	44.5	42.5	40.5	38.5	36.5	34.5	32.5	30.5
Soda ash	6.00	6.00	6.00	6.00	6.00	6.00	4.00	4.00	4.00	4.00
Soda niter	6.00	6.00	6.00	4.00	4.00	4.00	4.00	6.00	6.00	5.5
Fluorspar	6.00	6.00	6.00	6.00	6.00	6.00	6.00	7.5	7.5	5.5
Barium carbonate	–	–	–	–	3.5	3.5	3.5	–	–	–
Calcium carbonate	3.00	3.00	3.00	3.5	–	–	–	–	–	–
Cobalt oxide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Nickel oxide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Manganese oxide	1.5	1.5	1.5	1.00	1.00	1.00	1.00	1.00	1.00	1.5
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 4. Chemical analysis of indigenous raw materials used in various batch compositions of ground coat enamels for stainless steel.

	K.D. clay	Feldspar	Quarts	Lime stone
L/I	13.24	0.02	0.046	44.00
Al_2O_3	35.05	22.23	1.93	0.48
SiO_2	48.25	67.90	98.16	0.46
CaO	2.30	0.30	0.07	0.15
MgO	0.53	0.378	Traces	54.88
Alkalies	0.70	0.23	Traces	0.65
	–	9.14	–	–

very viscous and difficult to smelt down because of their high content of quartz and low content of fluxes. Enamels bearing 36-40 % borax had a decided tendency to crawl and the texture was not satisfactory. It is evident that the limit of borax is higher in the case of more fusible enamels. This may be due to the fact that the refractory enamels are comparatively viscous and this property is emphasized by the addition of borax.

Alkalies. The fluxes sodium carbonate and nitrate bring the refractories into combination in the smelting operation. They promote gloss but reduce opacity very decidedly. They have been used in all the ground coat batch compositions in Table 1, 2 and 3 in the proper proportion to get the desired results.

Barium carbonate imparts opacity and possibly reduces the solubility of the frit. It has been used in the batch compositions of ground coat enamels No. 3,13,14 (Table 2) for better results. Compositions high in barium carbonate showed poor smelting properties, the enamels bubbling and frothing to such an extent that crucible smelting was difficult. 6 % barium carbonate was sufficient to produce this tendency and 9 % aggravated it greatly. Composition No. 3, Table 2 containing 9 % $BaCO_3$ showed this behaviour during the melting of the frit.

Fluorspar in ground coat enamels should not exceed 7 % because excess of it may increase the refractoriness. When introduced in proper proportion, it imparts opacity to the ground coat and fluxes the batch. Fluorspar has been used in all the ground coat enamel compositions upto 3 % in Table 1, 4-10 % in Table 2 and 4-6 % in Table 3.

Lead oxide [3] has been used in ground coat enamel batch compositions from 1-5 % in Table 1. It promotes fusibility without materially reducing opacity, except by dilution. Litharge enamels show bubbling if it is used in excessive quantity. Compositions containing lead oxide from 4-5 % in Table 1 smelted excellently.

It is widely known that superior adherence of the enamel to the iron is obtained through a combination of cobalt oxide and nickel oxide [4]. In most commercial ground coat enamels, the sum of both oxides makes up about 1 % of the composition of the ground coat.

The paper from Sweden explains [5] that for good adherence, the enamel should be fired on in an oxidizing atmosphere. A thin oxide layer is required before the enamel flows; this helps the enamel to wet the metal surface. Iron oxides should be dissolved in the ground coat; the increases the thermal expansion of the enamel and also has depolarizing effect. Adherence promoting additions are, therefore, indispensable in the ground coat enamels.

In another foreign research paper [6] CoO and NiO and both have been used in the matrix ground coat, and the best adhesion is obtained with 0.25 % CoO and 1.25 % NiO.

Nickel oxide when added in the excessive quantity gave much bubbling. Composition No. 1, Table 2, containing 3 % nickel oxide bubbled through the ground coat. This defect indicates that bubbles in the enamel did not have enough time to escape properly. Gas bubbles or blisters can be eliminated by a longer firing period or a longer soaking period.

Manganese dioxide gives a good gloss and renders the enamels harder. When used with cobalt oxide in the enamel batch composition, a uniform colour is obtained. Manganese dioxide has been used in almost all the ground coat batch compositions listed in Table 1, 2 and 3.

Firing of the enamel. The ground coat is fired in a continuous [7] furnace. This permits better control of heating, economies of heat utilisation, and completeness of the structural change of iron. Gases have longer time to evolve and escape from the structure.

CONCLUSION

The study establishes that compositions containing 30-40 % SiO_2, 20-25 % feldspar, 25-30 % borax along with the constant additions of soda ash, soda nitrate, fluorspar, cobalt oxide, nickel oxide and manganese oxide have good mechanical properties. They are possibly tough, durable and highly thermal shock resistant. For example, compositions from 1 to 11 in Table 1 have developed superior adherence, better texture and gloss. Compositions bearing 45 to 60 % SiO_2, 20-25 % feldspar, 9.5 to 19.5 % borax with small contents of opacifier and metallic oxides are most refractory and smelt with difficulty at higher temperatures. They carry increased refractories and smaller content of fluxes. For instance, compositions containing 28-29 % SiO_2, 18-22 % feldspar, 30.5-35.5 % borax with minor additions of the other constituents are soft enamels and are fused at low temperatures: Enamels No. 2,7 and 2, Table 3, are softer, more brittle and have very little adherence. They are easily scratched and chipped off.

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