were worked out and put to the long term test in a bottle factory.

Procedure. In every fifteen minutes 2 kg of batch was shoveled out at the dog house and discharged alternatively into two boxes A and B. After separating the cullet by passing through 10 mesh sieve the dividing was carried out according to the following schedule.

In each step dividing was carried out by halving the sample size using the riffle samplar, larger or smaller according to the amount, and when the sample size was reduced to 600 g the sample was dried and milled for an hour in order to reduce the error caused by the dividing procedure.

Analysis. A simple volumetric method to separate the batch into three component, namely, soluble in water, soluble in hydrocgloric acid and the residue was adopted. The test with the mixture of pure chemicals has proved the high accuracy of the analytical method itself.

Precision. The variance, respectively, in sampling $\hat{\sigma}_S^2$, in dividing $\hat{\sigma}_R^2$, in analysis $\hat{\sigma}_M^2$ and the total variance for all procedures $\hat{\sigma}^2$ are given in the following table.

	Precision (%)			
	$\hat{\sigma}^2$	$\hat{\sigma}_S^2$	$\hat{\sigma}_R^2$	$\hat{\sigma}_M^2$
Soluble in water	0.0121	0.0037	0.0174	0.0001
Soluble in HCl	0.0163	0.0030	0.0310	0.0004
Residue	0.0370	0.0192	0.0405	0.0003

Time necessary for analysis. The total time necessary for carrying out the batch analysis by two operators war found to be about 13 hours. If only two final samples, each from A and B, were analysed the time necessary would be reduced to about 8 hours, although, at the same time,the precision would be lowered, for example, to $\hat{\sigma}^2 = 0.0225$ for water soluble component.

---

9. Effect of Vanadium Oxide on the Strength of Adherence of Heat-Resisting Enamel Applied on Nickel-Chrome Stainless Steel

Megumi TASHIRO, Sumio SAKKA and Hironori TERANISHI

(Sawai Laboratory)

Good adherence between the enamel coating and the base metal is particularly important for heat-resisting enamels, because the service conditions usually tend to accentuate stresses between the coating and the metal. Cobalt and nickel oxides,

which are generally used as adherence promoting oxides for porcelain enamels to iron base, have little effect on adherence between enamel and nickel-chrome stainless steel (K. Kautz, *J. Amer. Ceram. Soc.*, **19**, 93 1936). Therefore, the only method now generally used for the promotion of the adherence between enamel and nickel-chrome stainless steel is to make rough surface on the base metal by sandblasting or by severe etching with acids, which might result in the mechanical firm grip between the coating and the metal (Noda and Oya, *The Enamel Industry, Japan*, No. 9-10, 1952).

The method investigated by the authors is to use vanadium oxide as mill addition. The use of the proper quantity of this oxide assured the satisfactory adherence between the coating and the stainless steel. The stainless steel plate used was 0.4 mm. in thickness and has the following analytical composition : C : 0.04, Si : 0.96, Mn : 0.94, P : 0.033, S : 0.023, Cu : 0.36, Ni : 7.80, Cr : 18.05, Fe : 62.8. Before the application of enamel slip, the surface of each metal plate was cleaned at first by 10% caustic soda solution and then by 10% sulphuric solution. The computed oxide composition of frit used is SiO_2 39.0, B_2O_3 6.7, CaO 4.1, BaO 4.1, BaO 45.1, ZnO 5.1.

I. Selection of the most effective mill-addition for the promotion of adherence: Two (parts by weight) of TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3, CoO, NiO, ZrO_2, MoO_2, CdO, La_2O_3, As_2S_3 and $KMnO_4$ were respectively added to separate enamel slips, consisting of 100 frit, 5.5 clay and 0.2 $MgSO_4$. After thorough mixing, each slip was applied by dipping on both sides of the metal specimen 40×30 mm. in size and fired at 1000°C for about 3 minutes. Thickness of the coating was adjusted constant for all specimens (0.005 ± 0.001 mm. after firing). The coating of the above all specimens failed off partly or entirely from the base metal, immediately or at least within 3 days after firing, with the exception of the specimens applied with the enamel slip containing V_2O_5, MoO_3 and $KMnO_4$. Results of the falling weight test indicated that, of the above three oxides, V_2O_5 is most effective for the promotion of adherence. The addition of $KMnO_4$ caused copperhead deffect along the edge of specimens.

II. Optimum quantity of vanadium oxide as mill-addition : The enamel slips containing varying amount of V_2O_5 were applied respectively on separate specimens of stainless steel. The results of the falling weight test and the thermal shock test, which was carried on according to the method of Harrison (W. N. Harrison, *J. Research, N. B. S.*,**39**, 293 1947) indicated that the addition of 2 to 10 parts of V_2O_5 to 100 parts of frit is favorable for the good adherence. The specimen applied with the enamel slip containing such an optimum quantity of V_2O_5 remained unchanged even after quenched from 450°C into water.

III. Effects of addition of vanadium oxide on the oxidation of the base metal beneath an enamel coating: At high temperatures, oxygen in air diffuses through an enamel layer and reacts with the base metal. In order to know the effects of addition of V_2O_5 on this phenomenon, the rate of oxidation of the metal beneath an enamel

coating was measured by recording the progressive weight change with a sensitive balance on heating a specimenat temperature of 1050°C. The results are shown in the figure. The curves (1), (2) and (3) are respectively with a spcimen of bare metal,

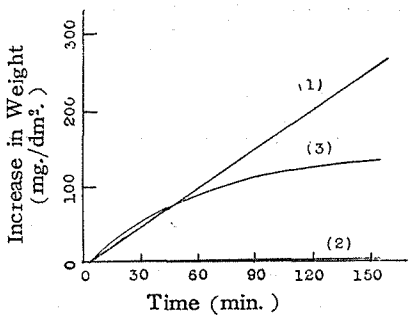

Fig. Effect of addition of vanadium oxide on the oxidation of the base metal.

a specimen covered with enamel containing 10 parts of V_2O_5 to 100 parts of frit and a specimen covered with enamel containing no V_2O_5. The results indicate clearly that the oxidation of the base metal at high temperature is suppressed by the addition of V_2O_5 to the enamel slip.

---

10. On the Synthesis of Alkylphosphonyldichloride

Ryohei ODA and Tatsuya SHONO

(Oda Laboratory)

Jensen (*J. Am. Chem. Soc.* **70**, 3880 (1948)) and Soborovskii (*Doklady Akad. Nauk S.S.S.R.* **67**, 293-5 (1949) : *C. A.* **44**, 1401) have recently reported a new method of preparation of organic phosphonyldichloride by blowing oxygen into a mixture of aliphatic or cycloaliphatic hydrocarbon with phosphortrichloride.

The authors have very much interested in these publications and studied this method with higher aliphatic hydrocarbons and examined at the same time the influences of temperature and of the molar ratio of hydrocarbon, phosphortrichloride and oxygen upon the reaction.

Table 1.

No.	Paraffin (g)	PCl_3 (g)	CCl_4 (g)	O_2 (hr)	temp. (°C)	P-contents (%)
1	80	35	100	2	Room temp.	0
2	40	35	0	6	50	0.3
3	20	35	0	12	50	0.69
4	20	52.5	0	12	50	1.13
5	20	35	0	12	75	0.36