INFLUENCE OF THE COMPOSITION OF FRITTED CERAMICS ON THE RESISTANCE TO ABRASION

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SUMMARY

Resistance to abrasion is and has been a subject widely studied by researchers and manufacturers of the ceramics sector to try and offer pavements that adjust to the growing requirements for quality in these products.

Studies carried out up to date have studied complex compositions resulting from the mixture of fritts and various raw materials.

The present work offers a study on the resistance to abrasion of different fritts and their modifications, always achieved by fusion. At the same time we establish a comparison of the same modifications achieved through the addition by grinding of different raw materials to the fritts.

INTRODUCTION

The action of mechanical wear on the surface of an object can produce the disappearance of small particles resulting in an undesired change in the aspect of said surface. This is known as abrasion and is valid for ceramics, metals, or any other material.

The search for the most wear resistant flooring is the object of ceramics manufacturers who try to offer high quality products, and with this in mind a series of experimental methods have been developped with more or less sucess. The manufacturers have tried to obtain information on the materials used and have attempted to use these results for the improvement of the finished product.

A method which is normaly used is the determination of the material's hardness - the resistance of a body to be penetrated by another. The simplest and best known way to measure this hardness is the Mohs trial which consists of submitting the material studied to a scratch test by a series of minerals whose hardness is known, so that the tested material's hardness is classified immediatly below in the hardness scale to that of the mineral which produced a visible scratch on its surface. The problems with this method are the influence the operator has on the final result due to the different

angle of the scratch or the pressure excercised in each case, and the difficulty of measuring appreciable differences amongst the majority of compositions as only the central values are usually used.

To avoid these problems in measuring the hardness the indentation method is used, in which the dimensions of the scratch produced on the surface by a pyramid shaped diamond point subjected to a determined force and for a certain period of time are measured. According to the shape of the indenter, there are different values of hardness: Vickers (square section), Knoop (romboidal), Rockwell (conical), or Brinell (steel ball).

The current, most accepted method is the one proposed by the Porcelain Enamel Institute (P.E.I.) because it gives results that are comparable with the daily wear produced on ceramic flooring, and this is the one that has been used in this study.

OBJECT OF THE STUDY

There are several works cited in the bibliography that are directly or indirectly related with wearout by abrasion. They are usually experimental studies that are destined to determine the effect on wear of some raw materials when they are added to ceramic enamels. We also found studies carried out with several commercial fritts usually used in the sector, studies that describe the resistance to wear and allow to compare the different compositions of each of the fritts with the values of wear obtained.

The wear is measured as the loss of weight (mass) suffered by the glaze, and it is obtained following the guidelines of the european EN-154 rules.

The present work studies the variations obtained in the wear by abrasion of a series of fritts representative of the families of fritts most widely used in the sector; through the study of the effects produced by a series of characteristic oxides when they are introduced in the fusion of the fritt, and later comparing the loss of weight of each of the fritts thus obtained. There is also a comparison with the wearout experienced when these same oxides are introduced in grinding.

We also supply data that may be useful in optimizing the fritts to improve their properties as well as chosing the adequate materials for making highly resistant enamels.

EXPERIMENTAL DEVELOPMENT

1- Five representative fritts commonly used in making typical pavement enamels either stoneware or not, have been chosen to carry out this study, they are:

A Zinc matt
B Calcium matt
C Transparent shiny doublecooked
D Transparent shiny singlecooked
E Opaque shiny singlecooked

TABLA DE COMPOSICIONES QUIMICAS DE LAS FRITAS

INFERIOR 15% ↓
SUPERIOR 45% ↑
15–45% ↔

FRITAS	Na_2O	N_2O	CaO	MgO	BaO	ZnO	PbO	Al_2O_3	B_2O_3	SiO_2	ZrO_2
A	↓	↓	↓	↓		↔	↔	↓	↓	↑	
B			↔	↓		↓	↓	↓	↓	↔	
C	↓	↓	↓					↓	↓	↑	
D	↓	↓	↓	↓		↓		↓	↓	↑	
E	↓	↓	↓	↓	↓	↓		↓	↓	↑	↓

The oxides used were:

Al_2O_2	BaO
CaO	ZrO_2
SiO_2	TiO_2

The fritts obtained are the ones resulting from melting the composition corresponding to each representative fritt, plus 5% and 10% respectively of each one of the above mentioned oxides obtaining a total of 65 fritts. The same number of enamels were obtained formed by the addition by grinding of the different oxides. In the case of Zirconium, barium and calcium we added the quantity of raw material (calcium carbonates and barium and zirconium silicate 5) necessary to produce 5% and 10% of the oxides.

The fritts were obtained by fusion in laboratory crucibles using natural gas as fuel and melting each fritt individually in cordierite crucibles providing approximately 3 Kilograms of fritt, cooling with water and drying.

2- The fritts were ground in laboratory ball mills with the following proportion in the charge:

Fritt	100
Caolin	5
Hexametafosphate	0.05
CMC	0.2
and 35% water.	

In the case of the materials added in the grinding the proportions in the charge were:

Fritt	100
Oxide	5 and 10
Caolin	5
Hexametafosphate	0.05
CMC	0.2
and 35% water.	

The enamels thus obtained were sifted with a ASTM 120 sieve and were applied by grinding at a pressure of 5 Kg/cm^2 and at a density of 1.6g/cm^3. We applied 8 gr. for difference in weight on pressed tiles of red stoneware paste of 11.5 cm x 11.5 cm with a first application of typical stoneware engobe. The tiles were single cooked in a 10 m. roller oven FORNIKER HFK-1.

The cooking reproduced the industrial curve for stoneware of 42 min at 1140°C of maximum temperature. After cooking, the dimension of the tiles were of 10.6 cm. x 10.6 cm adequate for carrying out the tests.

3- The method selected was, as has been said before the european rule En-154. We used a standard abrasimeter with an abrasive charge formed of 3 gr. of corundum FEPA 80, 20 ml of distilled water and 175 gr of steel balls with the following distribution:

70 gr	5 mm in diameter
52.5 gr	3 mm "
43.75 gr	2 mm "
8.75 gr	1 mm "

The test tubes were weighed in a Mettler H33AR scale of 0.1 mg of precision. After being cleaned and dried in the oven they were exposed to a temperature of 500°C for one hour in an electric muffler to eliminate any possible hydration water, weighing the test tubes again.

The results have been expressed in miligrams of weight loss of the worn enamel in each case.

RESULTS

1- We briefly summarize in the following tables some observations regarding the visual aspect of the pieces obtained.

Abreviations used:

B	Brilliance - shine
O	Opaque
M	Matt
T	Transparent
NV	No change
X	bubbling

ADDITIONS IN FUSION

ADDITIVE		AL_2O_3		CaO		SiO_2		BaO		ZrO_2		TiO_2	
FRITT	STD	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%
A	MT	NV	-M	B	B	NV	NV	-M	B	NV	O	NV	B
B	MT	-M	NV	NV	+M	+M	+M	B	-M	B	B	B	NV
C	BT	NV	NV	NV	NV	NV	-B	-B	-B	O	O	O	O/-B
D	BT	+B	M	NV	NV	NV	NV	NV	-B	O	O	O	O
E	OB	NV	+B	NV	-B	NV	NV	NV	-B	+O	+O	+O	+O

ADDITIONS IN GRINDING

ADDITIVE		AL_2O_3		CaO		SiO_2		BaO		ZrO2		TiO_2	
FRITT	STD	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%
A	MT	-M	-M	B	B	NV	NV	B	B	NV	NV	B	B
B	MT	-M	B	X	X	NV	NV	-M/X	-M/X	-M	-M	B	B
C	BT	NV	-B	X	X	NV	-B	NV/X	B/X	O	O	O	O/-B
D	BT	NV	-B	-B	M	NV	-B	-B	-B	O	O	O	O
E	OB	NV	NV	X	X	NV	-B	NV	M	+O	+O	-B	-B

2- Table I shows the results of abrasion obtained with the introduction of the different additives in the fusion of the fritts (the values represent the loss of weight in miligrams experienced in each case).

ADDITIVE		AL_2O_3		CaO		SiO_2		BaO		ZrO2		TiO_2	
FRITT	STD	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%
A	316	373	275	435	379	360	335	395	408	188	166	334	341
B	167	273	215	185	120	150	129	253	171	251	242	316	315
C	192	199	206	175	176	137	181	224	252	111	119	217	134
D	254	231	180	273	299	243	225	251	290	152	106	240	184
E	116	100	125	98	124	130	116	121	114	95	73	121	129

Table II represents the relationship between the loss of weight of each sample and the weight of the STD of each series. This value R is obtained in the following way:

$$R = \frac{\Delta P_{STD} - \Delta P_i}{\Delta P_{STD}} . 100 \quad (*)$$

ΔP_{STD} = the weight loss of the representative fritt of each series in mg.
ΔP_i = the weight loss of the different samples in mg.

ADDITIVE	AL_2O_3		CaO		SiO_2		BaO		ZrO2		TiO_2	
FRITT	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%
A	-18	13	-38	-20	-14	-6	-25	-29	40	47	-6	-8
B	-63	-29	-11	28	10	23	-51	-2	-50	-45	-89	-89
C	-4	-7	9	8	29	6	-17	-31	42	38	-13	30
D	9	29	-7	-18	4	11	1	-14	40	58	5	27
E	14	-8	15	-7	-12	0	-4	2	18	37	-4	-11

The results of table II are represented graphically (figures 1-6), the positive values indicate results in which the resistance to abrasion has improved with respect to the STD, and the negative ones represent a worsening.

ADITIONS IN FUSION

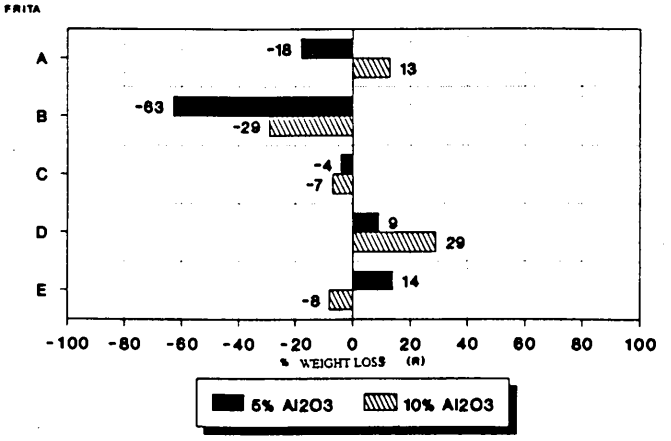

Fig. 1

The addition of Al_2O_3 produces diverse results depending on the percentage added and of the fritt tested in each case. The worst result was obtained with fritt B (calcium matt) with the addition of 5% which coincides with the appearance of a texture less matt than the original which seems to indicate that the Alumina favoured the formation of more vitreous phase, less resistant tha the cristaline phases. The addition of 10% provoqued a general saturation of Alumina which increases the resistance to wear.

The exception to this behaviour was experienced by fritt E that with the addition of 10% provoked an increase of resistance to abrasion. The observation of a shinier texture than STD seems to indicate the development of the vitreous phase which agrees with the results obtained.

ADITIONS IN FUSION

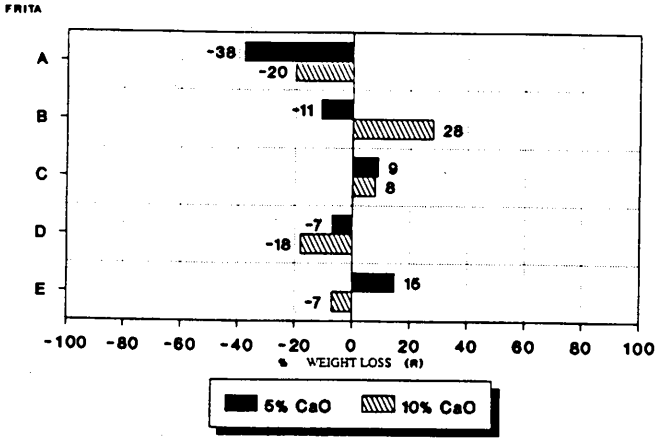

Fig. 2

The most important change provoked by the CaO can be seen in fritt A (zinc matt). The disappearance of the matt texture giving way to a very shiny effect indicates the development of a vitreous phase in detriment to the willemite crystalization (zinc silicate) which causes the matt effect on the original fritt.

In the case of fritt B (calcium matt) the addition of 5% of calcium oxide does not alter the texture significantly although it produces a slight reduction to resistance. The addition of 10% of CaO intensifies the matt effect which corresponds with the increase to resistance observed.

For shiny fritts the behaviour observed is somewhat irregular producing both improvements and deteriorations in the wear, however the variations with respect to the STD are not considerable.

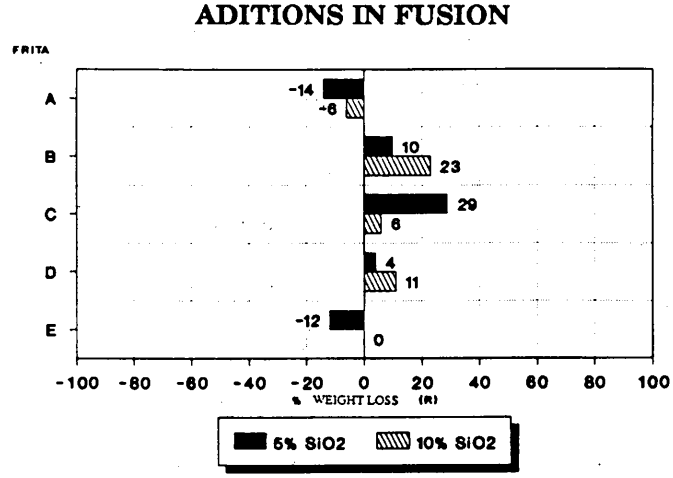

Fig. 3

Silica generally improves resistance to abrasion in all cases, but it is difficult to explain which is the mechanism because of the diversity of the compositions. In some cases it favours the separation of the crystaline phases from the vitreous matrix, a phenomenon which is usually accompanied by an increase in the resistance to abrasion of glass. In other cases, it is simply the saturation of the glass which prevents the total incorporation of silica in the vitreous phase and thus some of its crystals remain in suspension.

Surely it is this last mechanism which is responsible for the behaviour regarding wear when adding 10% of SiO_2. The exception in this case is produced with fritt A, where a first addition weakens the resistance but improves with the second addition although never reaching the same as the STD.

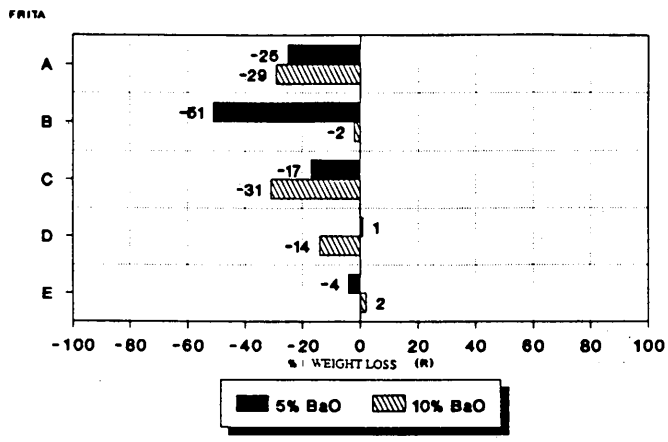

Fig. 4

The Barium oxide provokes a strong reduction in the resistance to wear. This result coincides with the observations found in the bibliography which indicate that the weakening of the structure of glass is more pronounced, the greater the volume of the modifying ion. The largest value of wear in fritt B appears with the addition of 5% of BaO which corresponds to a very shiny texture; this again confirms that the development of the vitreous phase weakens the resistance. The addition of 10% brings back the matt texture at the same time increasing the resistance.

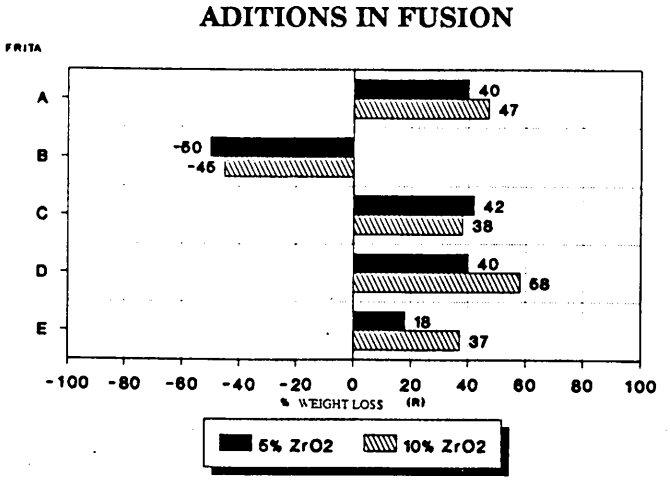

Fig. 5

We observed that the SrO_2 produced a significant improvement in all fritts tested, due to the crystalization of the zirconium silicate. In the case of the calcium matt the largest wear obtained together with the observation of a shinier and transparent texture lead us to suppose that the zirconium silicate is dissolved in the vitreous phase.

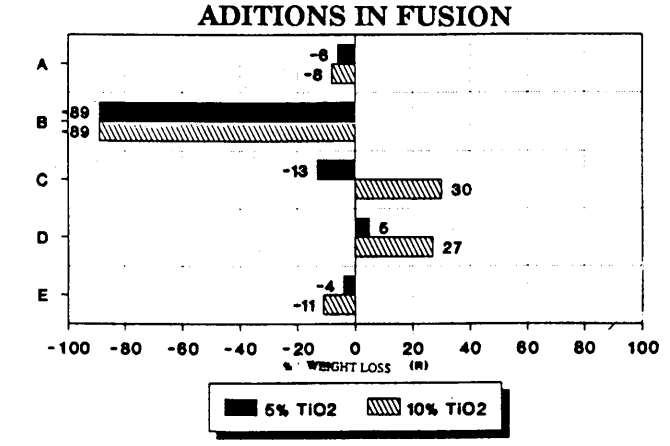

Fig. 6

In general TiO_2 provoked little variation to the resistance with respect to the STD, and in the majority of the fritts sudied the effect produced was of a reduction of the resistance, going against the resuslts initially foreseen and to the comments found in the bibliography. However, the most outstanding case was the calcium matt fritt whose worsening in respect to the STD was the largest of all cases studied. The tone of the enamels with the addition of TiO_2 is yellowish in fritts A, B, and C, and intense white in fritts D and E. This last is due to the support to becoming opaque given by TiO_2 when combined with the zinc oxide contained by these two fritts together with the absence of lead.

3 - Table III shows the results of the weight losses corresponding to the test carried out when adding the different oxides by grinding.

ADDITIVE		AL_2O_3		CaO		SiO_2		BaO		ZrO2		TiO_2	
FRITT	STD	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%
A	316	312	272	406	393	312	293	377	385	277	239	316	321
B	167	236	326	253	161	140	169	268	275	205	181	330	408
C	192	180	164	259	383	187	165	202	232	180	164	205	200
D	254	215	186	374	422	239	221	317	378	236	161	252	266
E	116	119	120	305	325	133	153	144	212	145	161	161	154

Table IV represents the values of the expression (*) corresponding to R for the addition of oxides by grinding.

ADDITIVE	AL_2O_3		CaO		SiO_2		BaO		ZrO2		TiO_2	
FRITT	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%	5%	10%
A	-1	14	-28	-24	1	7	-19	-22	12	24	0	2
B	-41	-95	-51	4	16	-1	-60	-61	-23	-8	-98	-144
C	6	15	-35	-100	3	14	-5	-21	6	15	-7	-4
D	15	27	-47	-66	6	13	-25	-49	7	37	1	-5
E	-3	-3	-163	-180	-15	-32	-24	-83	-25	-39	-39	-33

In figures 7 - 11 the data of the weight loss have been represented comparing the proceedures of fusion (Table I) and grinding (Table III).

FRITT A

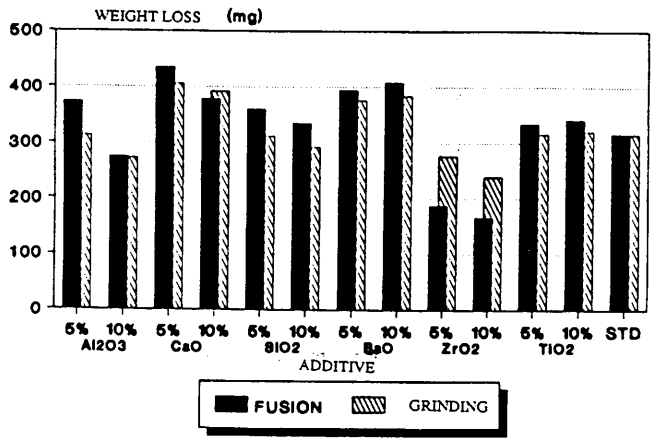

Fig. 7

FRITT B

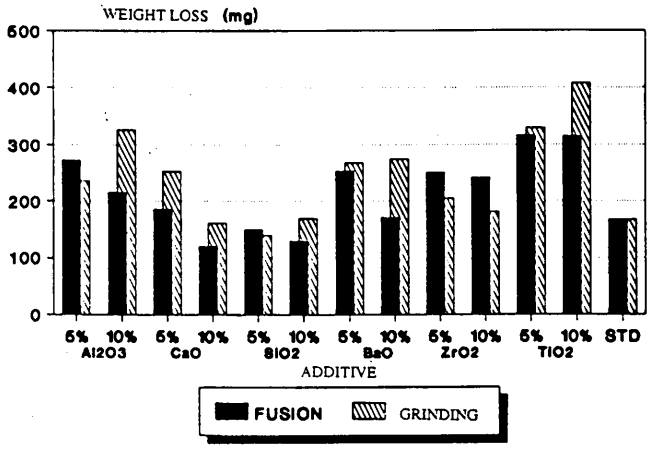

Fig. 8

FRITT C

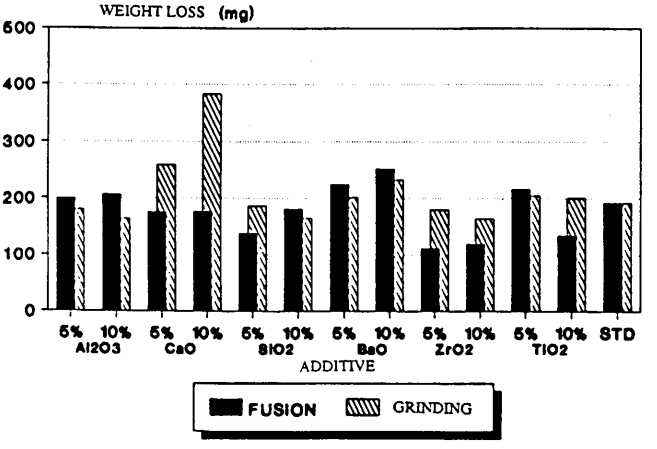

Fig. 9

FRITT D

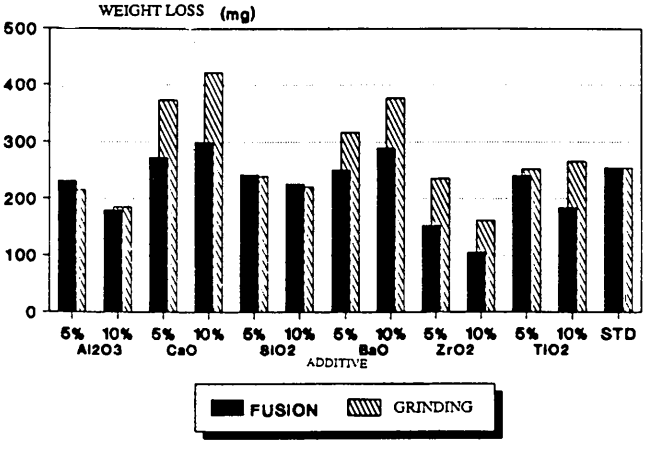

Fig. 10

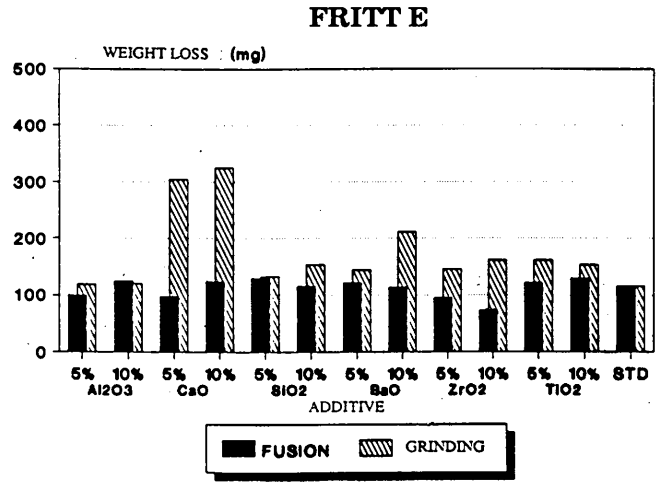

Fig. 11

In these graphs we observe that the results of the proceedure of fusion are in general similar or better that those obtained by grinding. Highly outstanding are the strong discrepancies of the results of the different methods in the case of the addition of calcium and barium; these discrepancies are undoubtedly due to the incomplete decomposition of the corresponding carbonates before the solidification of the glass inside the oven.

The lowest values in weight loss were obtained for the different variations on fritt E as was to be expected from the already existing data. Equally, the worst corresponded with the series of fritt A (zinc matt), in which the high percentage of lead in this fritt had a great influence.

CONCLUSIONS

Of all that has been presented in this study, we can conclude that there is no general behaviour for any of the tested oxides, but the effect produced by each one of them is the result of the composition and particular properties of each group of fritts. Thus, it is possible to find oxides capable of substantially improving the wear in a determined makeup of a fritt, and of producing the contrary effect with another fritt of a different makeup.

It is interesting to note those compositions for which we have obtained the lowest values of weight loss, that is, those that have the best resistance to abrasion. Notwithstanding the irregular behaviour, these results were:

* Fritts A, C, D and E with ZrO_2
* Fritts B, c and D with SiO_2
* Fritts B and E with CaO
* Frit C with TiO_2
* Fritt E with Al_2O_3

These compositions can be used for the development of enamels as well as for the obtaining of granulites with a high resistance to wear, being able to obtain a wide range of finishes due to the diverse textures offered by these fritts.

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