Effect of Different Percentages of Titanium Dioxide Additives on the Enamel Protecting of Steel Surface

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ABSTRACT
This work involves the development of ceramic coating to steel surfaces (enamel).This enamel high quality consisted of two ceramic layers to ensure excellent bonding with the steel surfaces. The first is called the ground coat which proved bonding between the steel base and the second outer layer called the cover coat. Various concentrations of TiO_2 were separately added to the mixture of the cover coat, resulting in to much better densification of the ceramic outer layer, the hardness, thermal shock resistances, and glossiness were improved also .Moreover this addition has raised the corrosion resistances of the ceramic in harsh acidic environment and at higher temperatures Also this enamel was used to protect the surfaces of steels which have various carbon content.

Key words: Enamel, adhesion, cover coat, corrosion resistances, Titanium dioxide.

تأثير إضافة نسب مختلفة من ثاني أوكسيد التيتانيوم على خواص طبقة طلاء (آلمينا) لحماية الصلب

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الخلاصة
يتناول هذا البحث تطوير طلاء سيراميكي وهو طلاء آلمينا ذات مواصفات عالية من ناحية التصاقه بسطح الصلب الكاربوني ويتكون من طبقتين الأولى تسمى طبقة الأساس . وهذه الطبقة عادةً تستخدم كمادة رابطة فقط بينها وبين الطبقة الثانية والتي تسمى الطبقة النهائية . أما بالنسبة للطبقة الثانية فتم دراسة تأثير إضافة نسب مختلفة من ثاني اوكسيد التيتانيوم على خواص طبقة الطلاء . ومن خلال الدراسة تبين أن هذا النوع من الطلاء السيراميكي يوفر مقاومة عالية للتآكل في الأوساط الحامضية القاسية ذات درجات الحرارة العالية إضافة إلى الصلادة العالية والانعكاسية العالية من خلال قياس اللمعان . ويمكن استخدام هذا النوع من الطلاء لحماية الصلب الكاربوني.

Introduction

Modem engineering technology, now demands some coatings which should also have a broad spectrum of effectively under a range of hostile environments. In recent years, dramatic improvements in properties of the glass-ceramic coating systems have been achieved by tailoring the microstructure of the glassy oxide coating matrix either by addition of secondary phases or by in situ crystallization

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of glassy oxide coating after application. Besides they required functional properties to suit particular end use requirements, the coating in general need to posses good adherence, defect free smooth surface and refractoriness [1-2]. It is also essential that the corrosion resistant coatings should possess high resistance to thermal shock, abrasion and impact damage in order to lessen the chances of failure due to reasons other than corrosion[3]. A vitreous enamel is classified as a ceramic material with many desirable properties which are generally associated with the ceramic family of materials, such as excellent general chemical inertness, high heat resistance, high surface hardness and resistance to degradation by ultraviolet light[4]. These properties are also combined with those more specific to glasses such as excellent ease of cleaning, and aesthetically pleasing appearances [5,6]. Enamels applied as a thin coating on steel is highly suitable for architectural panels, silos and equipment for chemical industry [7]. Vitreous enamel has a hard and abrasion resistance surface, a high resistance against high temperatures and thermal shock [8]. Furthermore vitreous enamel has a high chemical resistance and a hygienic surface. With enamel coating a long services life is therefore guaranteed which will eventually lead to a cost reduction [9]. Special high chemical resistance enamels were developed not only for the chemical industry but also for agricultural purposes like silos and stable floors [10]. Other interesting examples of technical usage are combustion chambers, stacks, sun collectors, industrial storage containers and tanks, pipes and exhaust pipes [11-14]. The present paper describes effect of different weight percentage titanium dioxide additives on mechanical and corrosion resistances of enamel protect steel coating. The coatings have been characterized and their properties have been evaluated as PEI and D.I.N. and ASTM standards. The coatings are designed for application on various grades of low alloy steel.

Experimental Procedure:

Low carbon steel substrates (20mm $\times$ 20mm) with (3mm) thickness whose chemical composition is measured by spectrometer instrument (Bergenalmer-W.G. in Materials Engineering Department – Technology University) as shown in table-1, are enamelled with a glass/ ceramic coat after being subjected to mechanical and chemical cleaning the later process normally leaves the metal surface with remnant roughness which promotes adhesion . The required glass/ ceramic (cover coat) frit was prepared from the oxides constituents listed in table-2, which were mixed properly and thoroughly then melted in a ceramic crucible in a furnace for 2 hrs at 1200°C. The molten glass is quenched in cold water fragmenting into coarse grained granules (frit). After milling the coarse frit some additives are added as shown-in table-3, to make a suspension (slurry) called the slip, suitable for application to metal surfaces by spraying gun. The sprayed surface is then left to dry in air , then fired at temperature ranging between (800°C and 820°C) for four minutes in order to enable the molten glass particles ,to melt and flow over the surface forming a thin glassy film adhered to the ground coat surface .

The test made throughout this work included the coefficient of thermal expansion of the glass/ ceramic coat measured by (dilatometer) are in accordance to ASTM standard (C539) [15]. The thicknesses' of the coats were measured using special device (Elcometer) Instruments. All adherence measurements were made in accordance to standard adherence tests issued by the Institute of Vitreous Enamels T29 [16], where test pieces should of thicknesses of 0.6 – 3mm for multi layers. The sample enamelled sheet is deformed by a punch with a hemispherical tip on to which falls 1.5 Kg mass dropped from a height which is a function of the thickness. In this investigation the height is (1 m) of the sheet prior to enamelling. This test evaluates the degree of adherence of porcelain enamel to metal in terms of the amount of metal exposed after standard deformation treatment, the indicator of adherence is the adherence index which is the ratio of the porcelain enamel remaining in the deformed area to that in the same measured area prior to deformation and is expressed as a percentage of the total deformed area. Thermal shock resistance test were made in accordance to ASTM 385.58 standard methods [15]. Moreover acid resistance tests were made according to DIN 51 157 standard [17] in corrosion laboratory (Chemical Engineerin Department- Technology University) , which is normally used in cases of enamel coatings. In this case the coating is exposal to solution of 20% concentrated sulphuric acid for 48hrs at 96℃. Micro hardness test was made on the ground and cover using the Vickers Micro hardness tester of Optical Microscope[18]. Hardness index measured by Shorsclorscope device. The Greek word sclor means hard, thus means the device which detects and measures dilution of a diamond-pointed hammer weighing (5g) which is allowed to fall from the standard height of 50 cm inside a graduated glass tube, the height of rebound is taken as a hardness index [18].

The porosity of the fired enamels (both open and closed) was established by using the following formula [19]:-

$$p\% = \left(\frac{W-D}{W-A} \times 100\right) \ldots\ldots\ldots(1)$$

Where P is the percentage porosity (%), W is the weight of saturated specimen in air (g), D is the weight of dry specimen in air (g), and A is the weight of saturated specimen in water (g).

The micro hardness test was made on the cover coat using the Vickers Micro hardness Tester of "LIETZ Optical Microscope W.Germany using following equation. The magnification was X100 , the applied load 300g and the time for impression was 20sec .The average of three readings of the indentation diameter, hardness was calculated using the following equation[18]:-

$$H_V = \frac{1854.4F}{d^2} \ldots\ldots\ldots(2)$$

Where H_v is the Vickers micro hardness, F is the loading in g ,and d is the impression of diagonal in μm.

The adherence index measurements were obtained in accordance with the standard adherence test of the "Institute of Vitreous Enameller T29and National Bureau of Standards. The sample enamelled sheet was deformed by a punch with a hemispherical tip on to which falls 1.5Kg mass dropped from a height 1m to the samples [16].

The adhesion strength test was made to measure the adhesion strength of the enamel coating of the test pieces accordance with the standard adhesion pull test of ASTM D4541. One enamel specimen was bounded to another through the epoxy adhesive, so measurement of the adhesion strength was conducted using Instron Universal Testing Machine type 2211 , the enamel specimen was pulled across head at speed of 0.5 mm/min, the shear loading produces the stress in a direction parallel to the interface . The specimen joint strength shear test is made by overlap joining [15].

The glossiness of all the samples was measured by the use of a Gloss-Meter ,Germany made. This instrument contains a stage of a black colour, where the samples were applied .First, the device was calibrated through control samples, then the sample was applied to the device, in an angle of 45^o. Then the reflection in the device was taken directly, the number given was a percentage according to the glossiness of each sample. The control samples have a glossiness of 90^o.

Table 1- Chemical composition of the metal substrate

Composition	Wt%
C	0.12
Si	1.21
Mn	1.29
P	<0.010
S	0.022
Cr	0.021
Ni	0.37
Mo	0.019
Cu	0.061
Al	0.055
Ti	0.069
V	0. 12
Nb	0.085
Co	0.068
W	0.017
Pb	<0.007
Fe	96.6

Table 2- Chemical composition of ground coat and cover coat

Formula	Ground coat Wt%	Cover coat Wt%
SiO_2	49.44	46
B_2O_3	20.5	12
Na_2O	18	8.5
F_2	1.63	3.5
K_2O	0.51	5.5
Li_2O	0.72	1.5
CaO	2.5	
TiO_2	5	12-28
P_2O_5		3
ZnO		2
CuO	0.3	
MnO	O.5	
NiO	0.3	
CoO	0.6	

Table 3- Enamel composition for (A) ground coat and (B) cover coat respectively

(A) Ground coat		(B) Cover coat	
Component	part	Component	Part
Ground frit	100	Ground frit	100
Kaolin	6	Kaolin	4
Borax	1	Borax	1
Water	50	Water	50

Results and discussion:

The porosity of thin layer was determined as a function of TiO_2 content as is shown plotted in figure-1.

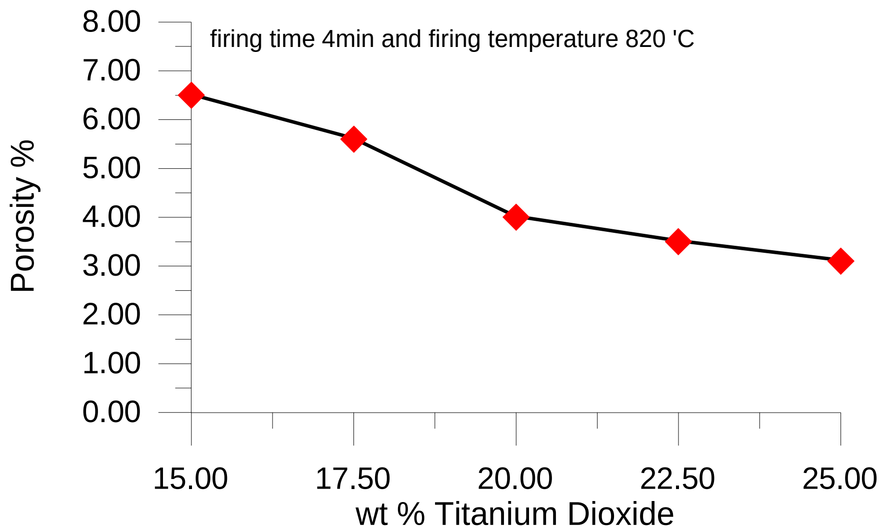

Figure 1- Relation between porosity and wt% of TiO_2

The porosity seems to decrease with increasing TiO_2-content because it is expected to enhance the surface tension and consequently other strength-related properties. The surface tension of molten glass is well known to be related to the froth. Formation process, and consequently the remnant pores density. This is expected of TiO_2 in glasses since Ti^{+4}-ions in any glass formation acts as network former which resides at network positions. This is expected to enhance the integrating of the glass as may be noticed from figure-2, which shows the variation between the hardness and TiO_2 content of the glassy enamel. The relationship is direct and higher Ti^{+4}-ions content enhances the hardness. Furthermore, the hardness may be considered as a measure of the mechanical strength of bulk of the material rather than the mechanical state of the surface. We may notice that the increment of 25 % TiO_2 has raised the hardness value about 25% of its original value when TiO_2% was minimum.

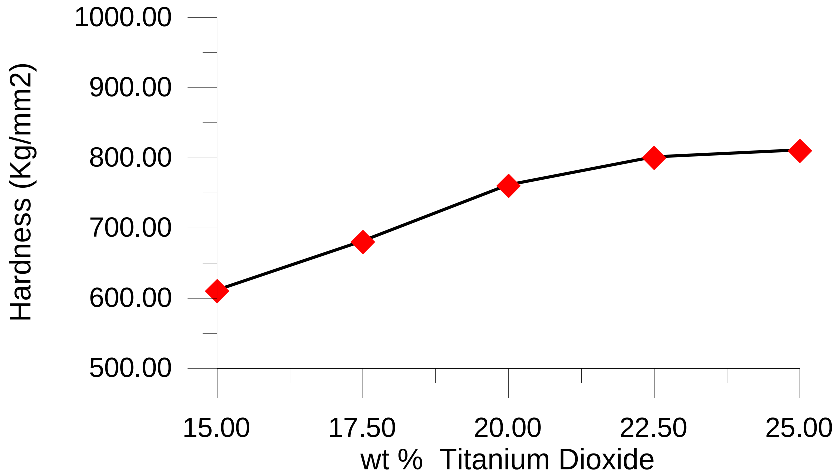

Figure 2- Effect of TiO_2 percentage on hardness of the cover coat

The adherence index of the multilayered ceramic coat is plotted in figure-3, as a function of TiO_2 content. This index is also enhanced by increasing TiO_2, which suggests that the impact resistance of this coat is also enhanced and that the resistance of the ceramic to mechanical spilling is improved. Because the improved or the strong glass to metal bond has a better elastic nature in conveying the mechanical impact energy.

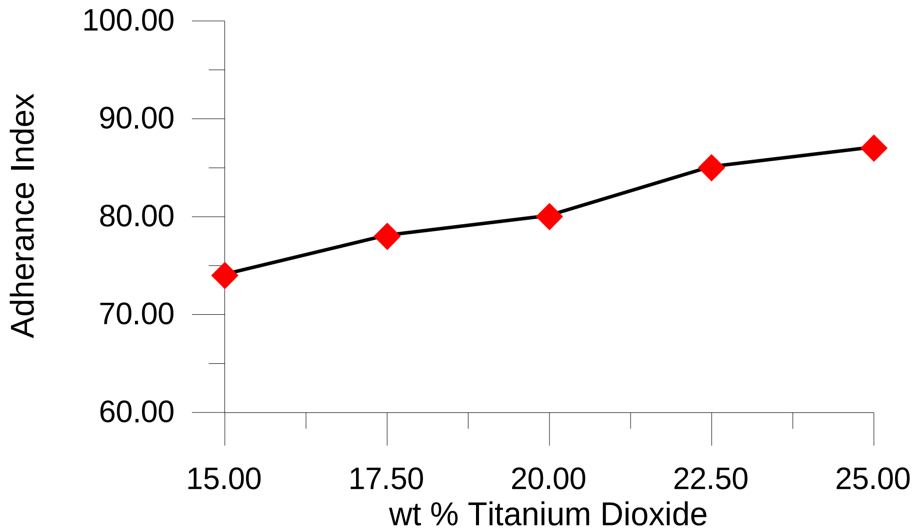

Figure 3- Adherence index as a function of wt% of TiO_2 for cover coat

On the other hand figure-4, shows the variation of the adhesion strength as a function of TiO_2 content of the cover coat glass enamel. Here also the increased presence of TiO_2 has enhanced the adhesion strength, which in fact is closely related to its wetting and bonding properties. Since the test is made by pulling the enamel layer of the base metal. This may truly represented the state of wetting and inter diffusion between the glass and the metal back plate, which is clearly shown in figure-4, to be enhanced upon TiO_2 addition.

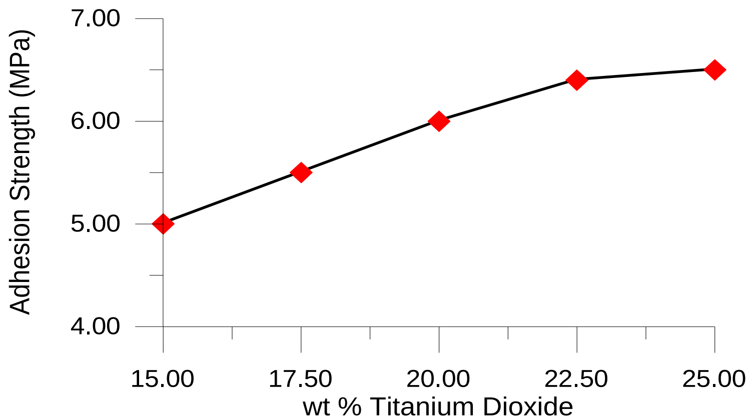

Figure 4- Relation between adhesion strength and wt% of TiO_2 for cover coat

Moreover, the thermal shock resistance is very closely related to the thermal expansion coefficient of the glass. And the addition of a network former enhances the mechanical strength of the glass. Hence an increased presence of Ti-ion enhances the thermal shock resistance of the glass, as shown in figure-5, which would suggest that this ion has improved the thermal compatibility of the ceramic-metal composite layered.

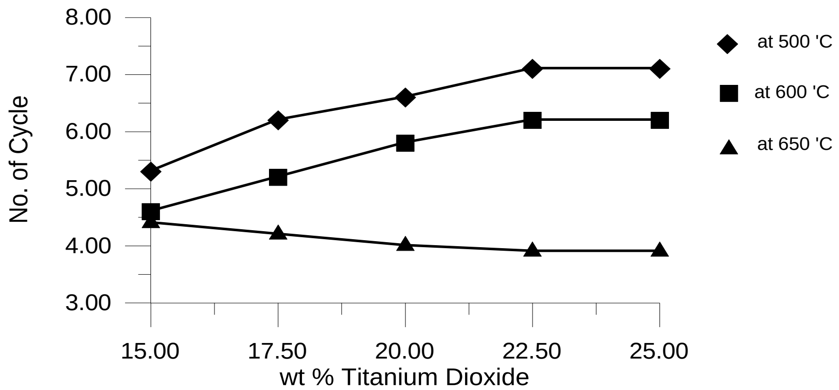

Figure 5- Relation between thermal shock resistance and wt% of TiO_2

The closer the values of the coefficient of thermal expansion of the metal base and that of the ceramic layers, the more compatible they are, and in turn the higher their thermal resistance. The thermal expansion of coated (enamelled) metal would result in a differential thermal expansion which may result in residual stress in the ceramic and the metal. These stresses may be added to those resulting from rapid cooling, which would enhance the possibility of failure of the bond. Since the shrinkage of a flat enamelled sheet may result in a net compressive stress in the ceramic enamel, and tensile stress in the metal. Such a situation is normally favourable because ceramics are known to be stronger in compression than tensile modes of loading. The above mentioned residual stress would enhance properties such as fracture strength and wear resistance. However, when the stresses become too great then failure may be in avoidable and may occur in the interface region of the bulk of the enamel. It may also be expected that the well-known difference in elastic module of metals and ceramics could lead to interfacial failure when the composite is subjected to applied stress or when there is a build up in residual stresses. And values of coefficients of thermal expansion of the various materials used in this work are shown in the table-4, for comparison. The rate of chemical corrosion of the double ceramic –metal layer was determined at various environment temperatures and plotted in figure-6, as a function of TiO_2% content. It's clear that the relationship is inverse which is in complete agreement with what is expected from network former ions, because stronger inter ionic bonding would enhance the mechanical strength and chemical resistance to corrosion. Hence Ti^{+4}-ions have increased the chemical resistance of the glass exposed to acids. This would correlate to the thermal expansion coefficient mentioned before and may be confirmed by the measurement of these coefficients for three separate glasses listed in the table-4.

Table 4- Thermal expansion coefficient (cm/cm ^oC)

Material	Thermal expansion coefficient (cm/cm ^OC)
Steel	12.56×10^{-6}
Ground coat (1% Co)	10.5×10^{-6}
Cover coat (20.5% TiO_2)	9.5×10^{-6}

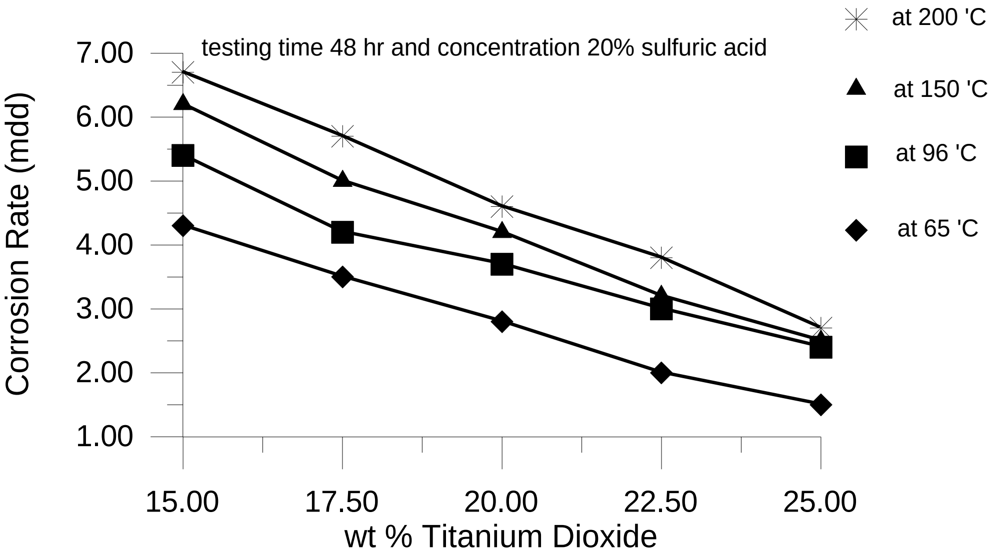

Figure 6- Effect of wt% of TiO_2 on corrosion rate at different temperatures

This in fact confirms the compatibility induced by Co-ion in the ground coat and the Ti-ion in the cover coat. The specific concentrations of Co and Ti ions were chosen because they mark the points at which the observed behaviour was stabilized. The closeness of these values listed in the table-4, above explain the observed thermal shock resistance and confirms the suggested mechanism by which Co-ions and Ti-ions act to consolidate the glass network of the enamel. This may be further confirmed by figure-7, which exhibits a comparison of the corrosion rates determined for the ground coat alone with that of three separate cover coats of different individual TiO_2 concentration. The cover coat with 25% TiO_2 is shown to reduce the corrosion rate by 43% at an ambient temperature of 65°C, and by 25% at an ambient temperature of 200°C. Thus suggesting its suitability for high temperature protection of metal surfaces.

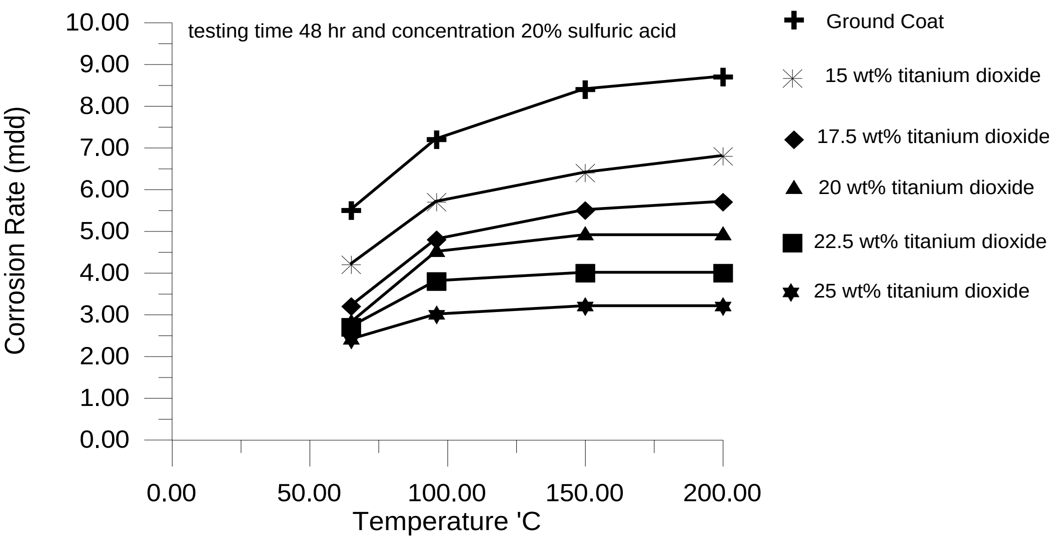

Figure 7- Relation between (mdd) and temperature of different enamel coatings

The glossiness of the above mentioned enamels were determined after being subjected to the above mentioned corrosion measurements and the result is plotted in figure-8,. The observed behaviour of set of curves suggests that higher TiO_2 content yields higher glossiness (reduction of corrosion), and that higher temperature yields lower glossiness values or (higher corrosion).

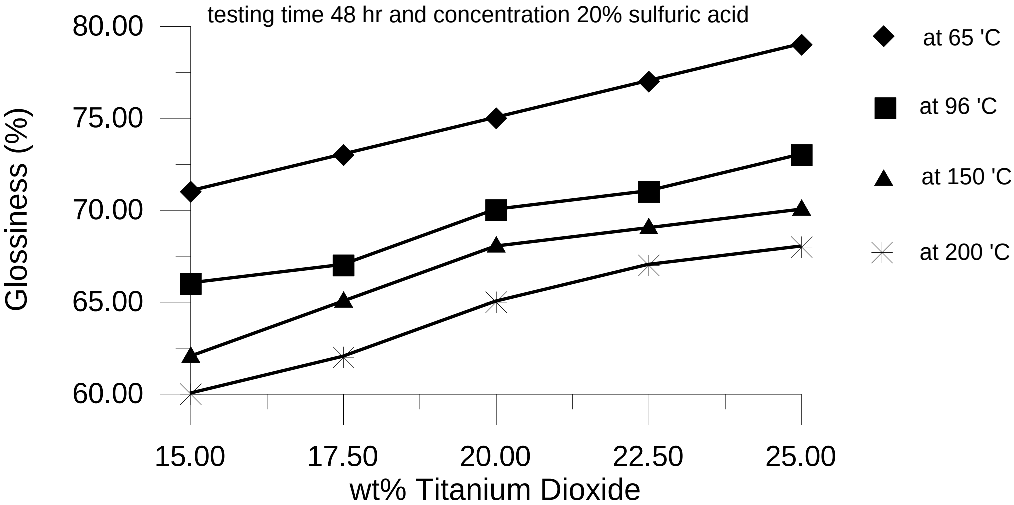

Figure 8- Loss of glossiness at different temperatures for cover coat

This would in turn confirm the decisive role played by the network ion in supporting, the chemical resistance of the glassy enamel. Restitution hardness is usually determined by measuring rebounding height l of a falling steel ball, which is totally dependent on the mechanical integrity of the bulk strength, and its continuity with the presence of any crack, porosity, or erosion .This rebounded height would tend to decline due to energy absorption or spelling of the surface. Hence, the term hardness is not really limited to the resistance of the surface to indentation or scratching, as it is traditionally defined. However, acid attack to the ceramic surface would leave it eroded which would enhance at higher temperatures or if the surface is roughened by porosity. figure-9, shows a set of curves exhibiting the variation of the restitution hardness of enamels containing different TiO_2%, and has been subjected to acid attacks at different temperatures.

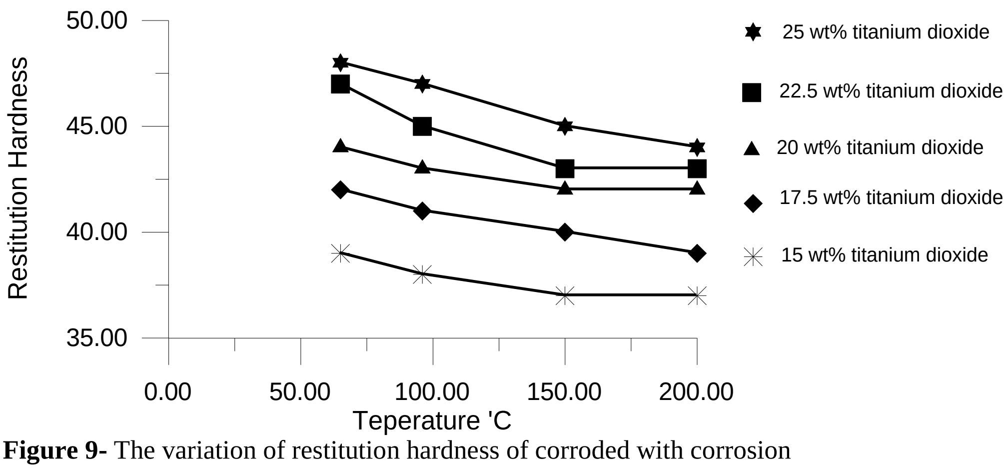

Figure 9- The variation of restitution hardness of corroded with corrosion

The overall behaviour indicates that higher temperature acid attack would result in lower rebounding heights or lower restitution hardness. This is very closely related to the degree of erosion inflicted on the ceramic surfaces, which is inversely related to the restitution hardness. Moreover, higher percentages of TiO_2% seem to exhibit a direct variance with the restitution hardness, which is quite explainable by what has been discussed above , since higher TiO_2% percentages have reflected quite positively on the properties of the cover coat especially where porosity is concerned. Also the observed enhanced density (reduced porosity) and adhesion with ground coat are expected to contribute to the overall homogeneity and continuity of the interface. This would in fact suggest that the various layers add more tightness and the enamel behaves as a monolithic coating layer.

Conclusions

1-It was found that Ti-ions in the cover coat enamel plays a direct and explicit role in enhancing the adhesion, acid resistance, hardness, and glossiness and moreover it reduces the porosity.

2- The cover coat with 25% TiO_2 is shown to reduce the corrosion rate and suitability for high temperature protection of metal surfaces.

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