Introduction

Under the term Porcelain or Vitreous Enamel for Chemical Industry has emerged in the last decades a composite material, because of its high chemical resistance, a firm place in the chemical industry. Many chemical processes depend on this enamel, numerous products can be produced economically only in enamelled equipment[1].

Because of its glass-structure[2], its high chemical resistant silica-glass in a solid melt-compound with the supporting steel lies the domain of Vitreous Enamel, traditionally reactions with acids at higher temperature used for chemical vessels, which could contain reactions with acids at higher temperature. Through further development of the Porcelain or Vitreous Enamel formulas and the technology, the original application-field has in the meantime substantially expanded, in other words, Vitreous Enamel is increasingly used to-day as an all-round inorganic material coating, also for contact with neutral and alkali mediums.

If the question regarding the resistance is raised, then one orientates easily at the values for acid and alkali, for example examined according to DIN-ISO 2743[*] or DIN-ISO 2745[*]. How Porcelain or Vitreous Enamel resists to the attack of pure water or generally the attacks of neutral water solutions, is often considered as less relevant one believes, that with a sufficient security referred to the acid or alkali reaction to be able to rely on inter-medium values.

With the technical background (Diagram 1) based on the results of earlier examinations with hydrochloric-acid and sodium-hydroxide [3, 4] it is possible to design an iso-corrosion-curve for the 0,1 mm/annum attack referred to a normal chemical enamel in the range of pH -1 to pH 3 and pH 10 to pH 14; connecting the two sections of the curve should appear the nearest approximation of the attack referred to a neutral watery medium.
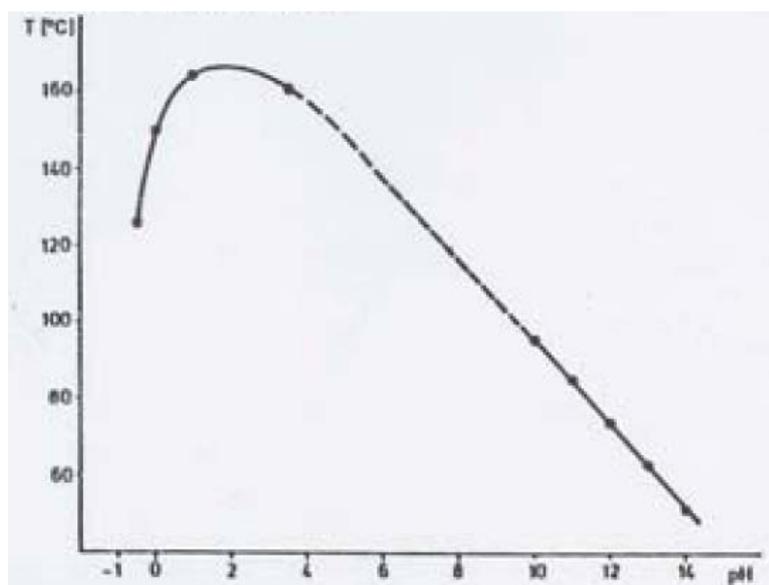

Diagram 1: 0,1 mm/annum iso-corrosion curve of enamel A referred to an attack with hydrochloric-acid (pH 1-3) and with sodium-hydroxide (pH 10-14); the area pH 4 – 9 has been interpolated.

The experience in the factory shows us, instead, that this procedure is only a rough simplification of the reality and does not reflect how Porcelain or Vitreous Enamel reacts to all the different neutral solutions in the industrial practice.

The aim of this study is to closely examine the reaction of chemical resistant Porcelain or Vitreous Enamels to water and neutral water- medium. Within the scope of this study should therefore the reaction of chemical resistant Porcelain or Vitreous Enamels to water and neutral water- medium be examined, in other words, the whole area of the water-attack should be investigated. The results of this study may serve the consumer of Porcelain or Vitreous Enamel to better understand the problematic nature of the corrosion mechanism and the tests referred to the requirements in the practise. Effects are indicated, which are theoretically not confirmed, but they do exist in reality and, as a consequence, here-of advice is given how through specific arrangements the efficiency of the enamelled equipment can be improved.

Theory

From a chemical point of view, Porcelain or Vitreous Enamels are like many other glasses can be considered as salts of polysilica-acids. The closed structure of the pure, polymer silica-glass, is in the Vitreous Enamel in part opened by the formation of salts with oxides of alkali and earth-alkali elements. The oxides of elements with values like boron (3) or zirconium (4), which are also components of the enamel, are generally built in the network of the silica-acid[1].

If such a complex compound is taken in contact with water-solutions[5], it does exist the tendency, based on thermodynamic principles, to hydrolyse completely. This process however at temperature under 100°C progress is still relatively slow and will furthermore be obstructed by the low solubility of some corrosion-products, this means that instead of a linear dissolving model, the glass- surface will be quite often loose the easier diffusing alkali-ions. The dissolved quantity of the Vitreous Enamel "ΔQ" versus time-unit " t" can be formulated with a simple rule:

$$(1) \quad \Delta Q = f\,(\,t\,)^{\,x}$$

In this way two ideal-conditions are characterized:

$x = 1.0$: the enamel is taken off in a linear way.
$x = 0.5$: the more mobile enamel leached material like alkali-ions have been washed out by the ion-exchange-system. There is the formation of silica-gel-layers on the enamel surface, which obstructs increasingly a further diffusion.

For this theory, referred to the acid and alkali-attack on chemical resistant Porcelain or Vitreous Enamel, exist already results, which do lead to the following situation:

i)   In the case of acids attack of Vitreous Enamel, at temperature around 50°C the exchange of ions reactions pattern dominates, e.g. the enamel surface is leached out, the wear off is insignificant. To estimate the resistance of the Porcelain or Vitreous Enamel this situation is of a little interest in the practice. At higher temperatures, instead, the polymer silica-dioxide will be increasingly split by the

action of the acid, and the linear wear off reaction models dominates, especially at temperature greater than 100°C.

Reactions scheme:

$$(2) \quad [M_2O_x \cdot ySiO_2]_{Glass} + H^+/H_2O \leftrightarrow y\, Si(OH)_4 \cdot aq + 2M^{x+} \cdot aq$$
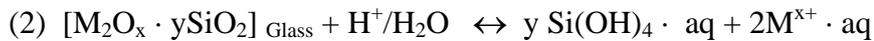
In this way, at a higher concentration of hydrogen-ions it is possible to have a high weight loss of 0,1mm/annum even with a chemical Porcelain or Vitreous Enamel at 125°C .
If the attacking acid has been enriched by hardly soluble silica-acid as a consequence of the corrosion or of specific additions, at these high temperatures will be build up on the surface a layer of silica-gel and the linear erosion model will turn into an ion exchange one[6].

ii)   In the alkali medium the polymer silica-dioxide will be transformed in a soluble silicate, at the beginning the enamel will be eroded, also at lower temperature, in a linear way.

Reactions scheme:

$$(3) \quad [M_2O_x \cdot ySiO_2]_{Glass} + OH^-/H_2O \leftrightarrow yHSiO_3^- \cdot aq + 2M(OH)_x$$

Therefore we do find in alkali-medium, with high pH-values, also in the case of more resistant enamels, even at 60°C an eroding value approx. 0,1mm/annum. As heavy soluble corrosion-products develop e.g. calcium-silicate and zircon-oxide-hydrate, which agglomerate on the surface as a protective layer. Similar as the acid attack reduces the value of erosion with the time of exposure[4].
The level of enamel-corrosion produced by acid and alkali determines the concentration of hydrogen respectively hydroxides ions. If one evaluates, the aggression attack of neutral water solutions, the corrosion-effect should be low, because the two types of ions are only present in a concentration of 10^{-7} mol/l. This can be confirmed by experiments e.g. in the case of a water-attack on glass it results practically only an exchange of ions, but when, as a consequence of the exchange of ions the concentration of hydroxide ions increases, at the same time starts also an increase of the hydrolysis of silicon-dioxide. This mechanism has been often described, confirmed and in principle accepted[5].

Reactions scheme:

$$(4) \quad [M_2O_x \cdot ySiO_2]_{Glass} + H_2O \leftrightarrow [H_2O \cdot ySiO_2]_{Glass} + 2M(OH)_x ; (x=1)$$
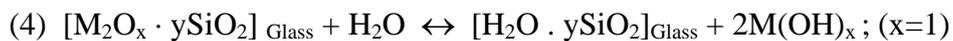
If one wants to put the theory into the practise referred to enamelled product-items, then a number of questions will arise:
   a) How much alkaline can water become, when it comes into contact with Porcelain or Vitreous Enamel?
   b) Is it necessary to use acid additives to avoid a threatening increase of the pH-value ?

   c) In an enamelled container is the liquid- or steam-phase more aggressive?
   d) Can, during the use of non volatile acids, the Vitreous Enamel in the steam-

phase be more than proportionally attacked by condensing water?

e) Can the results of the laboratory with fully desalinate water be referred to tap-water in the factory?

f) Are salt-solutions around pH 7 comparable in their aggression with pure water ?

g) There is a test DIN-ISO 2744[*], to determine the water-resistance of enamel. Which is the relation to the practise?

It would go over the frame of this paper to take a detailed position to all this questions with background information. There are however developed some single results with regards to enamel-consumer which offer important comments or also ideas for further trials referred to the individual requirements.

Test procedure

To carry out corrosion tests, as previously explained[3,4], it can be used either steel samples in the shape of a rod, enamelled on all sides with an useful open surface between 11 and 25 sq.cm or enamelled sample-plates (exposed surface 50 sq.cm), as described in DIN-ISO 2723[*]. The applied Vitreous Enamels A and B are of a different quality. A is a highly resistant normal trade chemical resistant Vitreous Enamel, B is a less resistant enamel grade for trials purposes, both falling in below oxide composition list.

Oxide composition List	
Oxide	Pecentage in weight (%)
SiO_2,	60-75
$(Li,Na,K)_2O$	10-20
$(Mg, Ca, Ba)O$	3-10
$(B,Al)_2O_3$	1-5
$(Ti, Zr)O_2$	3-10
CoO	0.5-1.5

As attacking mediums are used distilled water (conductivity < 0,5 µS) and tap-water. To be independent from any variation of the tap-water has been introduced a synthetic standard-water, which is freshly prepared for each trial: 800 mg sodium-hydrogen-carbonate, dissolved in 100 cc fully distilled water, are mixed under stirring with a solution of 500 mg calciumchloride-2-hydrate and 25 cc of chloride-acid 0,1n in 800 cc distilled water and this mixture has to be filled up to 1000 cc. The resulting "tap-water" has a pH-value of 6,8 and a carbonate-hardness of 20,3° dH (German Water Hardness scale). For any other salt-solution is used only p.a. - substances (p.a. = for analysis), and if not indicated otherwise, fully distilled water.

For trials under 100°C the enamelled samples and the medium are put together in laboratory bottles of polypropylene in a thermo-controlled water-bath to bring the items to the foreseen temperature. For trials at boiling-point, especially to determine the enamel-resistance to water-condensation at 100°C, the samples are installed in the equipment regarding (according) DIN-ISO 2733[*] and checked afterwards following the test-system DIN-ISO 2744[*].

For trials over the boiling-point, it is used an autoclave of high-grade-steel containing tantalum, Hastelloy C or PTFE (with a high-grade-steel case). After the test, the enamelled specimen are evaluated gravimetrically with an accuracy of 10^{-4} - 10^{-5} g-

decimal digit and by the loss of weight of the enamelled surface (sq. m.) versus the test time (d), in this way it is determined the surface related weight-loss V_K (g/sq.m.d.). Hence it is the possible to calculate the rate of weight-loss V_1 (g/sq.m.d) taking into consideration the specific gravity of Vitreous Enamel accounting for 2,5g/cm^3.

Results and Discussion

a) *pH-changing during the attack produced by water*

Starting from the ion-exchange-mechanism[4], we see, that the water attacks free alkali from the enamelled surface, which according to the following reaction hydrolyses the already leached-out protection-layer of silica-gel :

Reactions scheme:

$$(5) \quad [H_2O \cdot ySiO_2]_{Glass} + OH^-/H_2O \leftrightarrow yHSiO_3 \cdot aq$$

This interaction of ion-exchange and hydrolyses ~~can~~ , in the case of water-attack, can lead to a strong corrosion. Decisive for the extent of the attack will be the pH-value near to the enamel surface. This can be approximately determined by putting fine milled enamel powder in relatively little water and register the variation of the pH-value during the dissolving process.
To accelerate this process it should later be heated up (see Diagram 2).
10 mg of enamel A are put in 50 cc water, the proportion V / O of attacking water volume $V(cm^3)$ to the exposed enamel surface $O(cm^2)$ is about 0,25 cc/sq. cm.
At room-temperature results a rapid increase of the pH-value from 6,5 to 8,5: after heating over several hours in the PTFE- autoclave one reaches approx. a pH-value of 9,5. In a third action of hydrolysis at 200°C the pH-value is lowering down and approaches slowly a final value about pH 7,5.
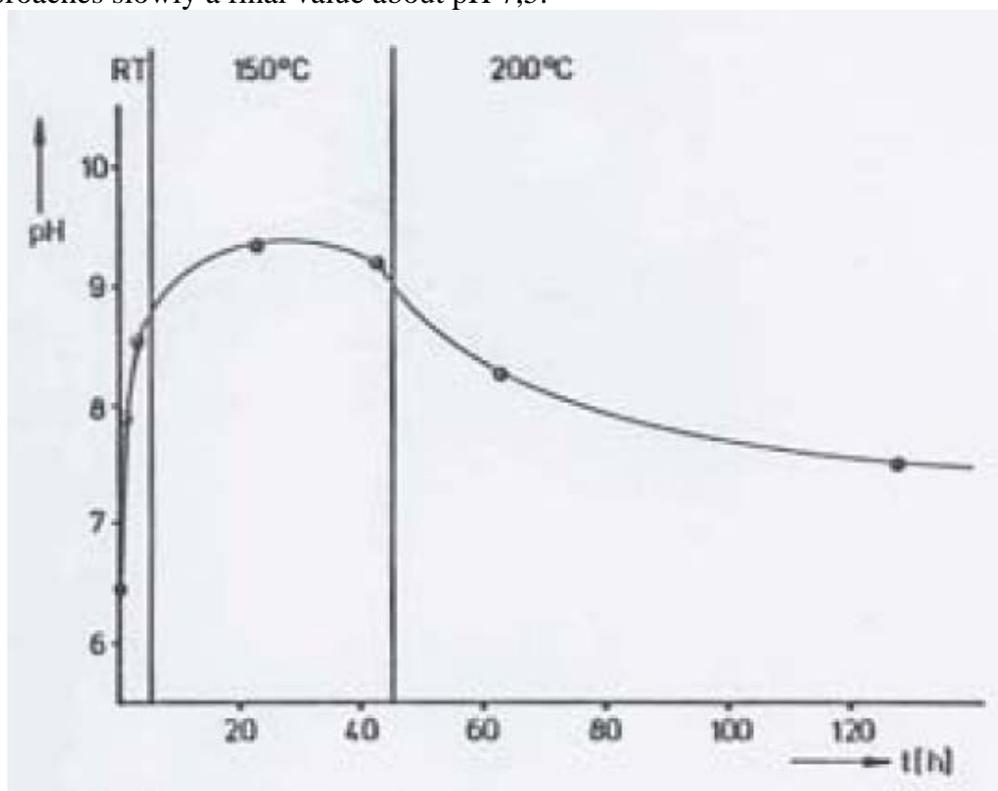

Diagram 2 :The change of the pH-value of water, which over the time **t** at different temperature (RT= room temperature) in contact with enamel-powder A.

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This trend corresponds to the expectation. After the wash-out of alkali and the increase of the pH-value, the network will also be dissolved, the pH-value falls when the alkali is neutralised. At the end the chemical enamel is completely dissolved, the pH corresponds at 7,5.

With this test it is possible to come already to the first conclusions for the practise. In the case of high Volume/Surface Rate or also with a steady change of the attacking water, the Vitreous Enamel Corrosion is not critical. In the unfavourable case with a small Volume/Surface Rate and without a change of attacking medium, the pH-value can rise between 9 and 10 at temperatures below100°C, but this alkali strength is considered only as a low demand. If one fears that this pH-drift, caused by the products of enamel-corrosion, could appear at higher temperatures, then a weak acid-addition to the water is sufficient to bring the pH-value to 3 - 4, to avoid this danger.

b) *Enamel Corrosion Test according to DIN-ISO 2744*[*]

In the case of a simultaneous attack of a test-sample by water in the liquid and vapour phase and in the steam-area, where by means of heat removal by the test sample, creating in this way a continuous condensate, should it be possible with DIN-ISO 2744[*] to determine the water-resistance in a representative way. Even in the case, that the condensation-attack moisten the surface only with a liquid-film and therefore the Volume/Surface Rate is small (about 0,05 cc/ sq. cm.) for the sake of a strong formation of condensation, the pH-value of the water in contact with the sample, not changes.
In the liquid- phase one registers an increase of the pH-value up to 9, because of the usual accumulation of the corrosion products.
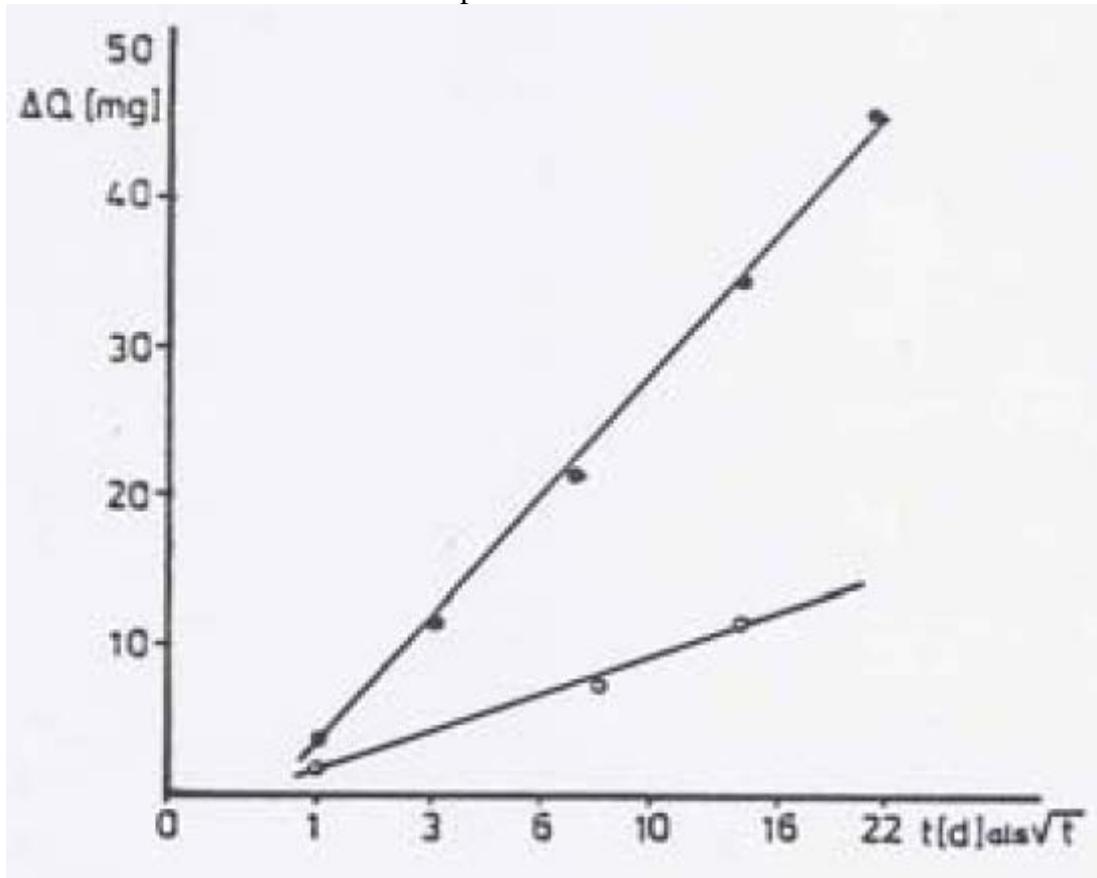

Diagram 3:Weight-loss ΔQ of the enamel A as a function of the test-time t resp. $\sqrt{t}$, determination with boiling water by DIN-ISO 2744 in liquid and condensate phase.

In Diagram 3 is shown the correlation between the weight-loss ΔQ of the less resistant enamel grade B versus time t. The regressions of the measuring points appear to be in a straight lines versus $\sqrt{t}$. This can be seen as a confirmation referring to the theory of the ion-exchange. The explanation for low attack of the liquid phase in comparison with vapour phase could be explained by the fact that there are in the solution the accumulated corrosion products of samples and glass-equipment at a low Volume/Surface Rate, which in spite of the increased pH-value lowered the attack. For the performance of enamelled equipment it is important, that only the sample, which has been attacked in the condensation-phase is decisive.

This "value of the vapour-phase" is in the first approximation valid for the whole reactor. The values for the liquid-phase, regarding DIN ISO 2744[*], are a particular case, because it would hardly appear in a chemical factory. The condensate-attack, regarding DIN ISO 2744 may be used to compare different enamel qualities. But in this case should be considered, that for the weight loss are used only values referred to the identical test-time, because of the $\sqrt{t}$. dependency.

This recommendation is not considered in the existing valid Norm.
Regarding DIN ISO 2744 the sample should as a standard-test be checked for two days and only in the case of a fall below the weight-loss-limit of 5 mg for each item, the 14 day test has to be applied. This rule offers additional advantages for the more resistant enamel, because it permits that, for example, a two days test for a weaker enamel is compared with the 14 day-test of the more resistant one. The inclusion of a relative comment referred to the exceptional case of the water-attack should be discussed in occasion of the next revision of DIN ISO 2744.

c) *Attacks of enamel by neutral water-mediums*
If not especially indicated have the trials described with enamel A experimented in a 1 day test and with a Volume/Surface Rate of 45 cc/sq. cm. in an autoclave with tantalum lining.

d) *Distilled water*
The Vitreous Enamel corrosion test with distilled water in autoclaves cause a lot of uncertainty and quite often confusing results, which were not sufficiently explained even by this study. It may however be allowed to comment, that this attack-medium, considered seriously, is hardly used in the practice and the questionability regarding the distilled water test should not be given too much importance. Already small additions of salts to the water, which are unavoidable under factory conditions, can cause completely different situations.

By means of the vitreous enamel corrosion test according to DIN ISO 2744 at 100°C one knows, that the water-resistance of a Chemical Vitreous Enamel is very good, the weight losses are generally lowered to 0,05 mm/annum. and in the case of high quality enamels also below 0,01 mm/annum (14th-trial). To determine a quality limit value, for example 0,1 mm/a, the trials have to be done in autoclave at temperature over 100°C. If during the test no inconsistencies appear , then one finds in the 1-day test with a large Volume/Surface Rate factor (90 cc/sq. cm.) and with a high resistance enamel like A, the weight loss at 140°C is about 0,02 mm/annum and at 160°C around. 0,05 mm/annum. When the gravimetrically determined weight-loss for each specimen results below 1 mg, it is possible that the values may scatter.

The pH value of the water remains, if measurable, practically unchanged between 6 and 7. This ideal condition proves however as very volatile, it means that insignificant modifications, which one quite often can hardly reproduce, could cause sudden increases of strong enamel weight-losses.

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One of the reasons could be, as also described in the literature for glass [5.7] that by the ion-exchange-mechanism the pH value of the water slowly increases. At a certain limit value the alkalinity is sufficient to change the corrosion attack model from the ion-exchange to a direct weight-loss; it means that the rate of the weight-loss is quickly increased. Low Volume/Surface Rate conditions, long Residence Times and higher temperatures underline this process. Therefore, can in an extreme case at a test with enamel A at 160°C the weight loss increase by a factor of 15-20 and reach values about 1 mm/annum. The same effect is probably to be expected, in the case of condensate attack under autoclave conditions, when finding relative high values of corrosion.

If one works, as in previous studies, with acid described[3] to use a relatively thick, enamelled plate to form the upper autoclave lid and the heating occurs in a vertical position, referred to the lower autoclave section together with the water, then forms a condensation at the not heated sample, because of the heat-loss at the autoclave-head. As the quantity of the condensate is limited, the liquid film would therefore hardly renew, but through the ion exchange increases the alkali-concentration and attacks the enamel strongly. At a temperature of 160°C on the enamel-surface the determined rate of weight-loss was about 1 mm/annum. In the general case of autoclave-trials, the content of dissolved carbon-dioxide has to be considered as an additional influence-factor. It has been demonstrated, working with distilled water, that the amount of weight-loss with a rate of Volume/Surface of 90 cc/sq.cm, at 140°C is about 0,015 mm/a, if the water has been boiled for 5 minutes before starting the trials. If however, an air stream was flashed for one hour through the water before doing the trials one did find a weight-loss of 0,064 mm/a under the same test-conditions. Probably with a small amount of carbon-dioxide a stronger corrosion starts (see also Section "k" and the drastic change to a higher weight-loss appears quicker.

e) *Strongly diluted acid and alkali*

If one works with strongly diluted acids, for example hydrochloric acid, pH 3 at 160°C, one determines a rate of weight-loss about 0,1 mm/a. During the test the pH value evolve up to pH 4. At 180°C results a weight-loss of 0,18 mm/annum with an increase of pH up to 5. These results are to be interpreted as follows:

The Vitreous Enamel start being dissolved according the first linear reactions mechanism[2] by the effect of acid, but when the concentration of hydrogen-ions is rather weak, the hydrolysis of the silicon-dioxide starts slowly and the ion-exchange[4] become predominant, hence the washed-out alkali neutralize the acid and the pH value increases.

On the reverse alkali-side, for example, with a sodium hydroxide solution at pH 9, at160°C, the weight-loss is 0,85 mm/annum as high as expected. One observes also here a pH-drift, but to pH 7,5 – 8,0. The interpretation will be similar as described above. The attack of a weak alkali-solution is buffered by a reaction of neutralization, this time by silica-acid leached from the enamel. One can, in this way, consider the attack nearer to the pure distilled water one and including the values of the weight-loss from Section "d" to define more precisely the characteristic of the curve of Diagram 1, hence obtaining Diagram 4.
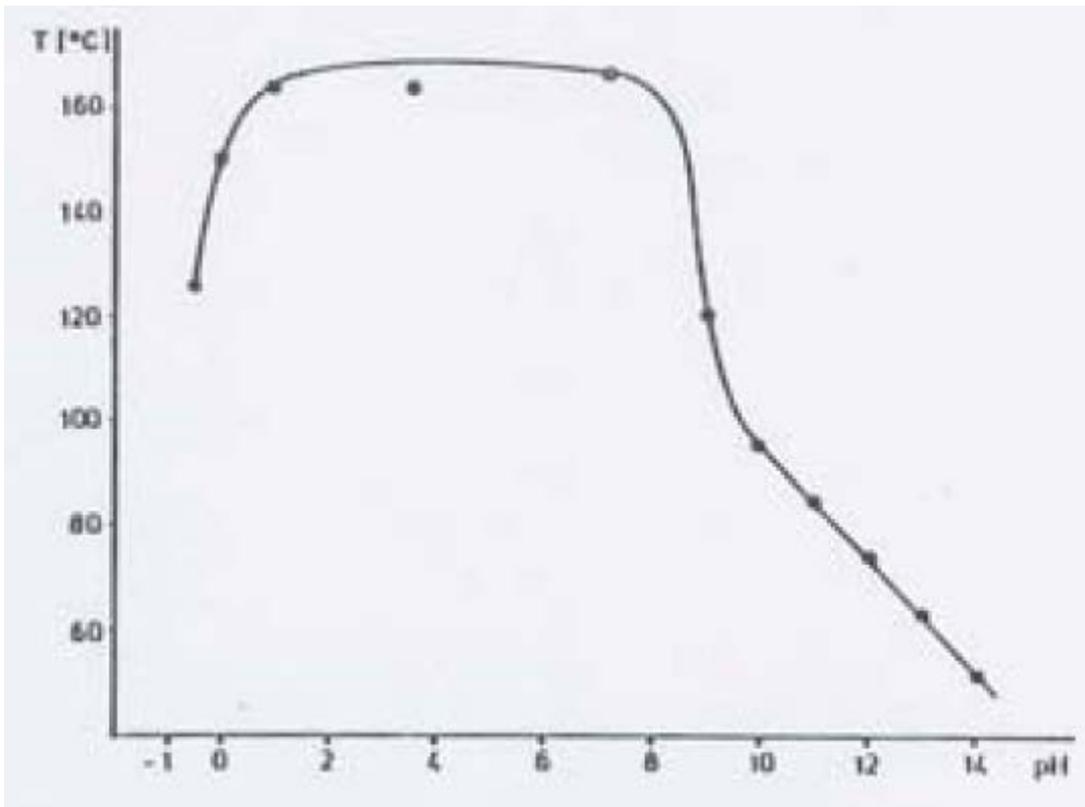
Diagram 4 : 0,1 mm/annum Iso-Corrosion Curve of enamel A referred to trials with hydrochloric acid, distilled water and sodium-hydroxide-solution.

Therefore, the resistance of the Vitreous Enamel from pH 2 up to approximately pH 7 is on a relative constant high level, between pH 8 and pH 9 it decreases in a drastic way and from pH 10 the curve does flow in the known slope of diagram 1.

The importance of these evaluations is however limited for the chemical factory, because each practitioner knows, that these ideally conditions do not exist in the production. The only balance with technical relevance will be, that operating an enamelled reactor with a mild neutral pH medium (like water), to avoid the risk of pH evolution towards higher value, to use a weak acid to neutralize the alkaline leached material from the vitreous enamel.

f) *Tap-water*

In contrast to distilled water, tap water contains a carbonate buffer that prevents the increase of pH value of the water due to enamel-corrosion-products, reducing the effect of the chemical attack of the vitreous enamelled surface. Nevertheless the corrosion of the enamelled surfaces by tap-water could be on a high level rate , due to the presence of some mineral salts in a dissolved state. When the influence of the Volume/Surface Rate and the test-time is low, the reproducibility is good. Regarding the corrosion temperature dependency, one can base on the rates of weight-loss for enamel A, correlated by the equation of Arrhenius.

$$(6) \quad V_1 \sim e^{-E_A/RT}$$

E_A: *Energy of activation*
R: *General constant of gas*
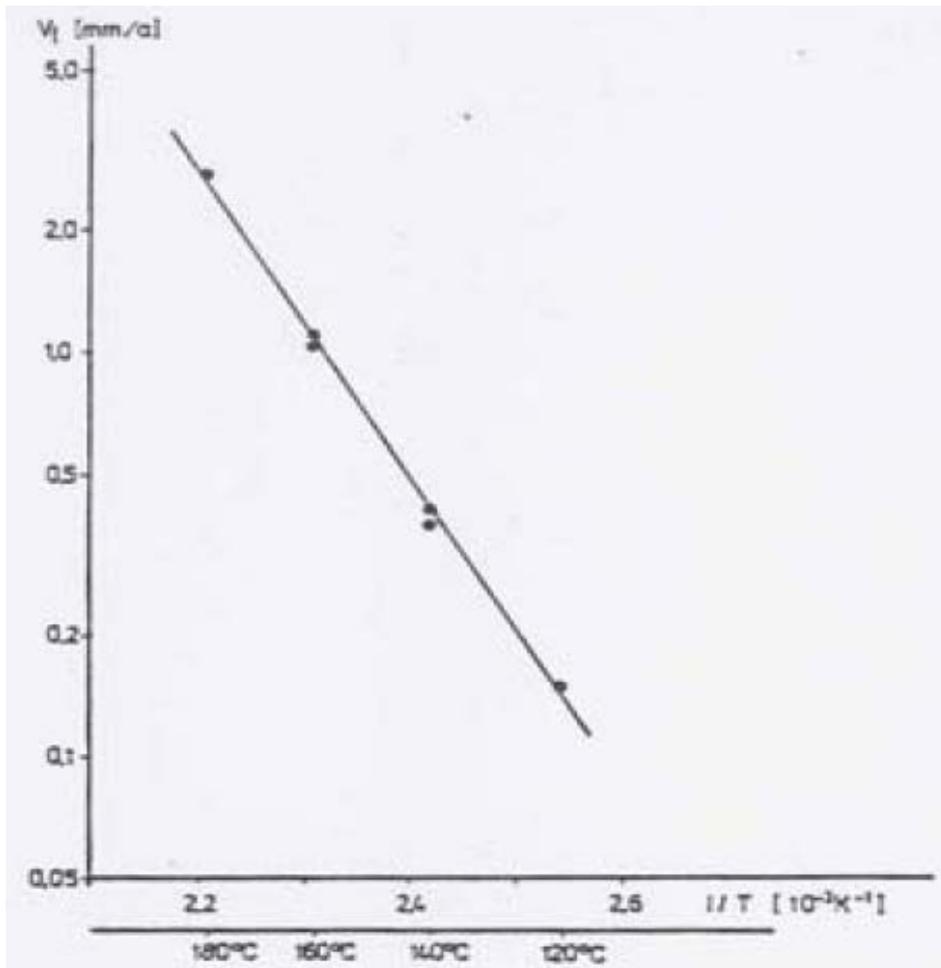T: *Kelvin Temperature($K° = C° + 273.16$)*

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Diagram 5: Rate of weight-loss V_1 in proportion of 1/T (T = temperature of corrosion)
enamel-attack by tap-water.

By the measuring the values one can calculate an energy of activation of
$$E_A = 71 \text{ KJ/mol},$$
it means, that in the considered temperature-range, a variation of the temperature by 15 K° the rate of enamel weight-loss increased by the factor 2. As shown in Diagram 5.

g) Salt-solutions
As the rate of enamel weight-losses increases by using tap-water, comes up the question of the "why". The answer can be given here as an approach in form of results clarifying corrosion-trials, which indicate the influence of dissolved inorganic compositions and their interaction.

h) Sodium chloride
Pure solutions of sodium chloride are slightly less aggressive than tap-water, but clearly more than distilled water. An example: at a concentration of 5 g/l and 160°C, weight loss amounts to 0,4 mm/a.

i) Earth-alkali-chloride
Calcium-chloride reacted neutral in the case of an acid attack[3] and exposed to an attack of a sodium-hydroxide-solution it even acts clearly inhibitive[4] but it is astonishing, that the pure solutions of calcium-chloride are very aggressive and in relation to the concentration they do exceed even the tap-water.
Example: With 1 g/l of calcium-chloride-2-hydrate, one reaches already at 140°C a rate of enamel weight loss of 1,4 mm/annum. Magnesium chloride and barium

chloride are approximately 25% and 50% weaker, respectively. In combination with sodium-chloride dominate the influence of calcium-chloride effect.

Example: With 0,5 g/l of calcium-2-hydrate plus 5 g/l sodium-chloride at 140°C, the rate of weight-loss 1,4 mm/annum.

Confirmation is also given with tap-water, which lost the carbonates by the use of hydrochloric acid and after the neutralisation with sodium hydroxide, one determines at 160°C a rate of weight-loss accounting for 0,85 mm/a

j) Aluminium sulphate

Out of literature is known, that the aluminium[3] reduces the attack of water, regarding the enamel we find: a water-solution of 1 g/l of potassium-aluminium-sulphate-12-hydrate causes at 140°C a weight-loss of 0.02 mm/annum; with a much-more aggressive tap-water one reaches only 0,1 mm/annum, (instead of 0,4 mm/annum without the aluminium-addition).

k) Carbon-dioxide and hydrogen carbonate

Similarly like carbonate during the alkali-attack, hydrogen-carbonate does work, in the neutral medium, with a corrosion increasing effect.

Example: a solution of 5g/l of sodium hydrogen carbonate does have a pH-value of 8,25. If one refers to the curve-characteristics regarding diagram 6, then should for a weak alkali solution with this pH-value at 160°C a weight-loss from 0,2 to maximum 0,5 mm/annum appear; in realty the attack, because of the solution of hydrogen-carbonate, increase the weight-loss to 2,7 mm/annum. Only by reducing the temperature to 90°C the value falls to 0,1 mm/annum.

Pure carbon-dioxide-solutions are relatively stable at higher concentrations; over 200 mg/l carbon-dioxide and 140°C result an enamel-corrosion below 0,05 mm/annum. Probably is in this case at pH 4 – 5, the in balance built concentration of hydrogen-carbonate too low, to trigger a strong attack. Small quantities of carbon-dioxide are more dangerous. The carbon-dioxide is neutralized by washed-out alkali, the pH-value increases, then hydrogen-carbonate are formed and the attack is speeded up. Example: water with 20 ppm carbon-dioxide at 140°C leads to 0,3 mm/annum of weight-loss.

l) Boric-acid and alkali-borate

In the investigated concentration area of 1 – 5 g/l the neutral solutions of borates do act
aggressively like tap-water, it means, that for the trial at 160°C results a corrosion-rate of approximately 1 mm/a.

m) Phosphates

Neutral solutions of phosphates do act surprisingly strong corrosively on enamel in relation to the concentration and temperature can the attack be stronger compared to phosphoric acid;

Example: a 5% solution of potassium or sodium hydrogen phosphate with a pH 7 at 80°C erode 0,24 mm/annum while a solution of 50% erode 0,50 mm/a.
In diagram 6 is shown the pH dependency of the vitreous weight loss under the attack of a 0.1% phosphate solution at 120°C.
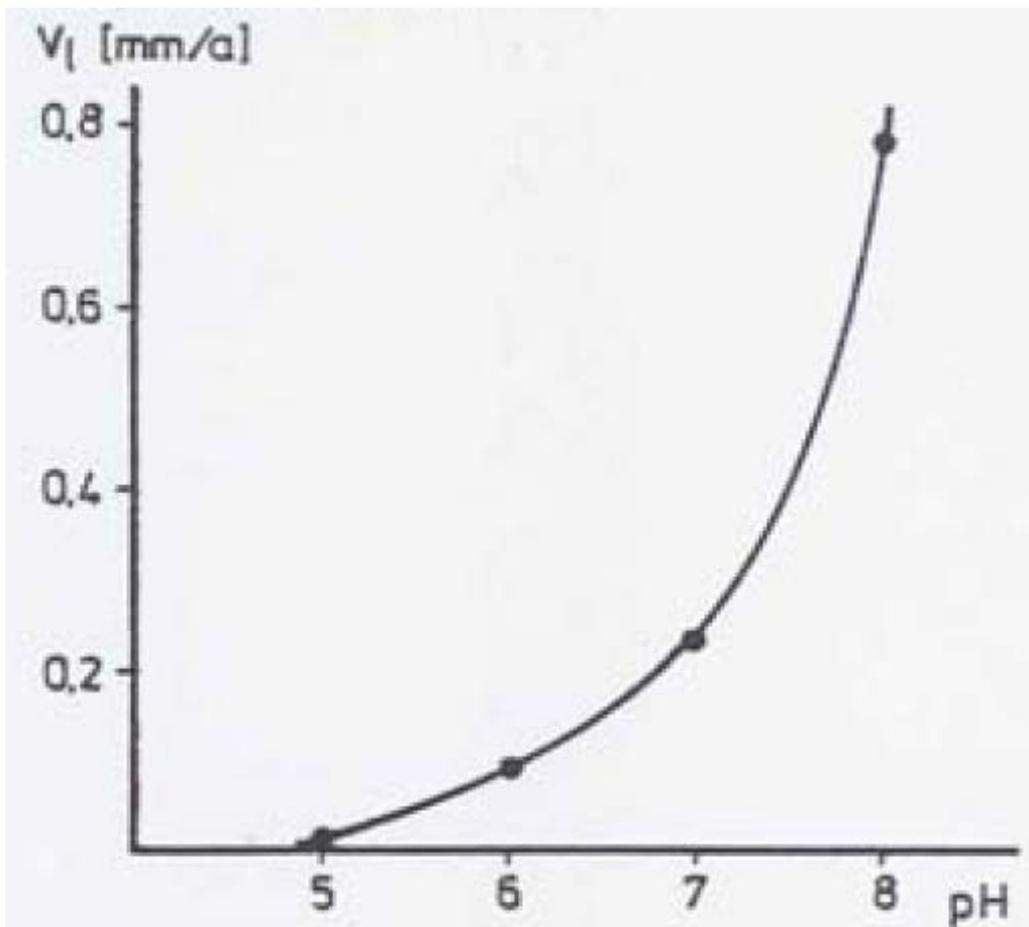
Diagram 6 : *Rate of weight-loss V_1 in proportion to the pH-value of a 0.1% phosphate solution at 120°C.*

In stronger alkali-solutions the attack of phosphates and alkali are overlapping[4] but the level of weight-loss is increasingly characterised by the alkali-solution; at pH 14 the presence of phosphate leads only to an increase of about 20%.

Similarly to other strong-corrosive-mediums, regarding the enamel, is also in case of phosphate the proportion of water decisive regarding the attack. Phosphorus-pent-oxide or phosphates dissolved in water free medium (sulphuric-acid, phosphoric-acid, and acetic-acid) do practically not attack the enamel; this refers to concentrations about 20% at 100°C. But the literature[10] does give indications, that from 200°C upwards concentrated solutions of phosphoric acid, probably by the formation of pyrophosphates, course a strong glass-dissolving effect.

n) Silicon-acid

By the addition of small amounts (in ppm) of solid silicon-acid in a fine dispersed form, for example Aerosil ®, it is possible to inhibit strongly the acid attack on enamel[6,] while in alkali-solutions this the effect is relatively weak[4]. In the neutral-area it shows, that in the case of pure ion-exchange-reaction, the already low values of weight-loss can hardly be influenced by additions of silicon-acid. But if the vitreous enamel matrix has been attacked and the rates of weight-loss are therefore high, the effect of silicon-acid is very positive.

Example: At 140°C and an addition of 1 g/l Aerosil can reduce the weight-loss of tap-water from 0,4 to 0,013 mm/annum.

o) Hydrazine

In the chemical-factory one uses instead of fully desalinated water, also condensate water from the steam generator, which often could contains small amounts of hydrazine. A trial with 0,01% hydrazine in water (pH 9,5) indicate, that the small amount is already sufficient for a strong attack at 120°C with a weight-loss of 0,75 mm/annum. This value is higher than expected, referring to diagram 4, but it is in line with the results, which have been identified with diluted solutions of ammonium[4].

p) Condensing steam from water-solutions of heavy -volatile compositions

If in a chemical-factory are boiled, for example, water containing sulphuric acid or salt of hydrochloric acid, should in the vapour-atmosphere theoretically be only [the] condense of water and at 100°C apply in first line the value of DIN-ISO 2744[*]. But if the solutions of heavily volatile compositions in the DIN-ISO trial presented in the liquid phase and boiled, one recognizes after the evaluation of the samples, taken out of the condensate, that this simplification is not permissible. Probably during the boiling-process small amounts of the heavily-volatile composition splatter up, so that the rate of weight-loss does not refer to the water-attack, instead corresponds to a heavy diluted liquid-phase.

Example for a 2-Dimentional (2^{-d}) Statistical Trial:

Enamel A	V_1 (mm/annum) in the vapour-sphere
Liquid-phase:	
Fully-desalinated-water	0.013
0,1 N Sodium-hydroxide-solution	0.150
5 g/l Sodium-hydrogen-carbonate	0.100

Enamel B	V_1 (mm/annum) in the vapour-sphere
Liquid-phase	
Fully-desalinated-water	0.130
Tap-water	0.200
Sulphuric-acid at 20%	0.080

For the factory-practice the result of these trials can be considered positive on the whole.

In the case of heavy volatile acids one notices a formation of condensates with a pH value lowered to 7, by which a possible alkalisation via ion-exchange will be efficiently neutralized. With strong corrosive mediums, such as sodium-hydroxide, the attack in the liquid phase is anyhow more critical, it means, the buffering action of the condensate is of a secondary importance.

q) Water with organic compositions

In the case of an attack with neutral water, solutions with many organic chemicals compositions react indifferently, only some solvents might reduce the corrosion-effect. Organic Compounds with a lower boiling point than water, for example methanol, one may consider in addition, that the temperature of condense formation is lower. Enamel B will be attacked by condensed water regarding DIN-ISO 2744[*] as follows:

Results:	V_1 (mm/annum) in vapour phase
Distilled water	0.130
+ 10% methanol	0.032
+ 10% ethanol	0.070
+ 10% n-propanol	0.060
+ 10% n-butanol	0.082
+ 0,3% azethylazetone	0.061
+ 0,5% methylisobutylketone	0.100

r) Alternative attack   acid – water

In the same equipment DIN-ISO 2733[*] is used alternatively without taking off the sample, 1 day test regarding DIN-ISO 2743 with hydrochloric acid at 20% and 1 day regarding DIN-ISO 2744 with water. The values of the samples exposed to the condensate-attack are controlled after 4 days.

Result: in the first approximation an influence caused by the change of medium does not exist.

Results of the tests	Rate of weight-loss V (mm/annum)	
	Enamel A	Enamel B
a) DIN-ISO 2743[*] (2d-test)	0.042	0.190
b) DIN-ISO 2744[*] (2d-test)	0.013	0.130
Medium Value of a) and b)	0.028	0.160
Result of the alternative-test With acid (S) and water (W) (1dS + 1dW + 1dS + 1dW)	0.030	0.140

Summary and Conclusion

During the attack with pure water a glass will be only leached out. It means, that the cations of the glass, and here again the alkaline ions in preference, which are exchanged with hydrogen-ions of water molecules. On the enamelled surface a layer of silica-gel is formed in this way. This process of ion-exchange carries on undisturbed until, through accumulation of the alkali-ions, either in the building-up layer of gel or also in the attacking water increasing   the   pH value of the solution, so that the ion exchange mechanism turn into a considerably stronger alkali attack one.
At the time when the change to a higher weight-loss commences, depends on several parameters; it will be intensified by a small proportion of attacking water volume referred to the exposed glass-surface, a longer contact with the same medium, a weaker glass quality and higher temperature. If the attacking water is slightly acidified it neutralises the alkali-action at the beginning and avoids the undesired change in the mechanism of the attack. These well known facts out of the literature one can confirm in principle also for the Porcelain or Vitreous Enamel.
Example: the pH-value of the water, which leached out the enamel for a longer period, can in extreme cases increase the pH-value up to pH 9,5 and starts therefore the drastic change to the alkali-attack. On the other hand it is possible to reproduce, either at a high Volume / Surface Rate or also by a continuous change of medium, as in DIN-

ISO 2744[*] with a sample in the condensate-test, the exchange of ions with a low weight-loss rate. In accordance with the theory (diffusion controlled ions exchange mechanism) the validity of the "time dependency law" has been confirmed, it means, the weight-loss of a sample increased proportionally to the square-root of the test time.

This ideal condition of the attack with pure water is likely to be mentioned as a starting point when one generally estimates the reaction of a chemical Porcelain or Vitreous Enamel compared to neutral water, technical medium. If one follows however the question in an experimental way, for example, how tap-water or mineral salts water solutions will attack, it will be found after a quantitative evaluation of the samples, that the above indicated, simple way with pure water leads too far from the practice and in many cases results in the estimation of too high a resistance of the enamel.

Because of the complexity of the inter-relation regarding the enamel-corrosion by neutral-water-mediums means in the single case, that concrete statements can be achieved only by corrosion-trials, in which the conditions referred to the practice have been realized to a large degree. In the following have been indicated some reference points and trends referred to the action of single components of water solutions, which can appear in a chemical factory. From the normal tap-water, it means, a weak carbon-dioxide-hydrogen-carbonate buffer with small amounts of sodium and calcium-ions, the enamel will be attacked much more than by a fully-desalinated-water. This depends on the presence of different dissolved mineral-salts such as sodium-chloride or calcium chloride. Surprisingly also neutral solutions of hydrogen-carbonate and phosphates are aggressive, which can not be totally explained by the existing theories.

Positive for the Porcelain or Vitreous Enamel are on the other hand aluminium[3] and additions of silica-acid to the water, which is also known from the literature for glass. In the beginning, when it is in contact with the enamel, already reacts slightly alkaline. So can water with 0,01% of ammonium or hydrazine already cause a typical alkali-attack with high weight loss. Organic additions to the water are generally favourable, the rate of weight-loss are here mostly lower compared with solutions of mineral-salts.

The influence of the temperature on the vitreous enamel corrosion by neutral-water-mediums is in all cases approximately identical. The rate of weight-loss can be correlated via the absolute temperature by the Arrhenius equation; the energy of activation results as approx. 70 KJ/mol. Therefore, the variation of the temperature for each 15° K to calculate with a double or half of the rate of weight-loss. How are these results judged under the aspect of transferability of the test technical conditions to the industrial practice? The test-method indicates short test-times, and a practice-related, relatively high Volume/Surface Rate. In this way is secured that the statements of the liquid-phase attack can be transferred directly.

For the attack in the vapour phase, for example of an enamelled container, the proportions are slightly more difficult, if one starts with pure-water; here the test-time and the Volume/Surface Rate play a very important role. It is difficult from the beginning to judge, how the attack of the enamel will develop, because there are sections where a condensate will form, where it runs back preferably or where it may stay longer in niches without renewal. However the trial indicates, this dilemma does not exist under factory conditions, because in the practice the condensate phase is not a pure-water.

Even water solutions of heavy volatile chemicals compositions like sulphuric-acid or sodium-hydroxide appear in very small quantities in contact with the condensate (probably mechanically through spatters during stirring and boiling). For practical considerations should therefore in the case of estimating the vapour-phase-corrosion one has to start from the assumption that the condensate attacks as a "strong diluted liquid-phase". If one takes into consideration, that an alkalisation of the condensate would be possible, then a small amount of a suitable volatile acid should be added in the liquid-

phase. It is favourable if organic products like alcohols come in contact with the condensate, in the case of the easier volatile compositions the temperature of the condensate-formation is lowered down, which decreased also the rate of weight loss. In this connection may be mentioned, that many compositions which attack the enamel heavily in a water solution, are hardly active in a water-free medium.

Example: sodium-hydroxide in alcohol or phosphate in sulphuric-acid. The critical point of such solutions is naturally, at what water content the corrosion noticeably increased. Fixed rules do not exist for different systems, but the experience teaches, that water solutions with concentration below 1% are not important, but a definite statement can be reached only by precise trials.

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