THE POSSIBILITY OF THE APPLICATION OF THE CLAY-FREE ENAMEL SYSTEMS IN THE PRODUCTION OF THE ENAMEL-COATED CHEMICAL EQUIPMENTS

Emil Barta, Lampart Vegyipari Gépgyár Rt., Budapest, Hungary
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Both increasing quality requirements and economical aspects in connection with enamelled products call for realisation of new technologies which try to minimalise or eliminate the using of clay and different ingredients, partly because presence of this is unnecessary partly because the presence of this cause unavoidable substandard quality.

This tendency spreaded and become successful mainly at the enamelling of products made of thin sheet (combi-smalt).

Technologies working well on the other fields can't be used in the enamelling of chemical equipment because of the specialities of the technology and the products.

In the production of enamel-coated chemical equipment traditional enamelling is used. The enamelling in wet system application is done by spraying of the enamel slip which always contains clay and set-up salts.

The quality requirements appearing in the field of the production of enamel-coated chemical equipment force moving towards the direction mentioned above. The main task is to eliminate of the negative effects caused by clay-system to build a more homogeneous and reliable coating and it should of course still be economical.

The characteristics of the enamel slip

The enamel slip consists of solid particles of one or several frits above 90%. For the traditional wet process the frit is ground wet in ball mill. Suspending agents must be added into the slip to avoid sedimentation of the enamel particles. Clay is the suspending agent.

Clay minerals are the products of nature so they are not homogeneous compounds. According to the chemical composition they consists of 40-60% SiO_2 and 20-40% Al_2O_3. They always contain crystal water and organic impurities. Under given circumstances there are 5000 times more clay particles in the slip than frit particles.

For this reason behaviour of the clay is strongly deciding the suspension's properties. The slips and the coating properties are influenced by the type and the quality of the ingredients.

The effect of clay on the enamel slip

In addition to providing necessary technological properties of the enamel slip the presence of the clay causes many negative effects.

- Increases the firing temperature
- Degreases the anticorrosion properties
- Degreases the stability of the enamel slip

The clay as natural raw material shows different particle size and cation exchange capacity whereby the rheological properties of the slip are influenced.

The enamel surface as every silicate-glass is attached by water. Depending on the chemical composition this alkaline wash is continuous. Therefore the rheological properties of the slip change continuously. Dissolved materials can't be removed. They remain in the slip and cause defects.

The rheological properties of the enamel slip are influenced by the following factors:

- The quality and the quantity of the clay
- The quality and the quantity of the inorganic salts
- The degree of alkaline wash

The effect of clay on the enamel structure

Certain amount, size and distribution of bubbles are developed during the firing of the dry enamel coating. This is the enamel structure.

The presence of the bubbles is important because they serve balances of expansion arising from different expansion-coefficient of enamel and steel and adsorb the gases.

Bubble free enamels are vitreous, brittle, too many or large bubbles cause poor chemical and mechanical resistivity of the surface.

The following causes bubbles:

- The evolution of closed air during the firing
- Leaving of combined water on the surface
- Decomposition of organic materials being in the clay
- Dehydratation of clay (400-500°C)
- Oxidation of carbon content of steel (600°C)
- Reaction of water vapour and hydrogen

Different clays but even clays coming from the same deposit lose their crystal water either in a part or as a whole in wide range of temperature which lead to further uncertain source of defects.

The water vapour coming from the clay reacting with carbon-monoxide lead to hydrogen formation increasing the gas content of the coating just when this has the lowest viscosity. So the high clay content causes enamel defects.

Our aim is therefore to have small and middle-sized bubbles spread evenly trough the structure. This kind of bubble structure fixes the hydrogen coming from the steel-enamel interface and makes the coating elastic without influencing the chemical resistivity.

The structure of the enamel is determined fundamentally by the mill additions especially by the clay.

The effect of the clay on the characteristic properties of the coating

Resistance to the chemical attack

The function of clay is to surround the frit particles, so the frit particles are in the network built by clay particles. This results solving of the clay in the frit during the firing influences its composition resulting increasing the amount of Si and Al ions. The undissolved particles will be some kind of intermediate material.

Clay is able to show their suspension effect in the presence of set-up salts so this salts changes the original frit composition.

It can be stated that the presence of the clay and set-up salts lead to decreasing of chemical resistivity.

Mechanical properties

The effect of clay on the mechanical properties can be traced back to the effect on the bubble structure. The presence of clay is not necessary because required bubble structure is not due to the presence of the clay but come from the nature of gas reaction.

Uncertain particle size, composition and chemical reactions of clay during the firing have a rather negative effect on the bubble structure.

Thermal-expansion coefficient

By the leaving the clay out from the system the value of the thermal-expansion coefficient, the transmission temperature and the softening temperature may change. These changes would be different according to the character of the frit system.

According to our measurements in clay-free system the value of the thermal-expansion coefficient is

unchanged or rising slightly, the transformation temperature is unchanged.

Thermal shock resistance

The function of clay in systems with clay is to fill out the space between the frit particles. In a system without clay change of thermal-expansion coefficient can change the thermal shock resistance too.

The effect of clay on the technological parameters

As we explained before the clay has its positive function in the system but causes instability of rheological properties. The presence of clay raises the firing temperature.

After the spraying and drying the clay-water type slip form a compact and easy to tear coating. This contributes to strain lines forming during the firing.

The using of clay-free systems

The aim of the clay-free system application is the elimination of negative effects caused by the clay. The other aim is developing on enamel system and technology, which goes a long way to eliminate one special problem, the strain line formation during firing.

This requires a technology, which enables the formation of loose structured dry enamel coating behaving flexible during firing. This can be partly achieved by hot spraying in the clay-water system used at the present time. But the implementation of this is uneconomical and unreliable. The problem can be solved in a suspending agent (not clay)-water-alcohol system. In such a water-alcohol system evaporation of water can already be urged while spraying thereby an almost dry surface can be reached with unlimited thickness without being soaked and with a loose structure.

A suspending agent suitable for this technology should meet the following requirements:

- Prevention of sedimentation of frit particles
- Ensuring the adequate rheology
- Strengthening of dry enamel coating
- Full decomposition during the firing
- Forming of a suitable bubble structure
- Non-toxic effect
- Supply of the suspending agent in standard quality
- Compatibility with water and alcohol
- It can be used in low concentration
- Show stability in relation to pH-variations, temperature variations and concentration variations of dissolved salts

Technological conditions of application

- Dry milling
- Ensuring identical grain size distribution in a given size range
- Hermetic mixing system ensuring perfect dispersion
- Hermetic spraying system
- Furnaces ensuring gradual heating up

Advantages of application

- Alkaline wash as a result of wet grinding can be avoided
- Elimination of rheological instability
- “Ready to Use” application
- Suitable particle size can be ensured

- Elimination of uncertain gas formation coming from the clay
- Improvement of coating properties
- More economical production

Number of persons have been concerned with the possibility of application of clay substituting agents. There were efforts to substitute clay either in a pert or as a whole using other clay minerals and organic high polymers. Some of the materials didn't ensure the requires rheological properties for a change over without problems, other proved unsuitable because of their behaviour during the firing.

One impediment of ensuring of positive result was the considerably short firing time, which hindered the full burning of the additives from the system.

In spite of these were materials with which successful results were ensured. The considerably long firing times applied in the enamelling of chemical equipment eliminate the difficulties mentioned above.

To sum up we can say that it is possible to do enamelling in traditional wet system without clay. On the basis of our positive results can state that it is possible to product enamelled chemical equipments by applying clay-free systems and we have to be concerned with this topic to be able to develop a technology with which we can product more effective, more sure, more reliable, more economical equipments with better coating properties.

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