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PROJECT DP/CPR/89/001 - DEVELOPMENT AND APPLICATION OF COATING TECHNOLOGY

FINAL REPORT REGARDING THE TRAINING OF THE GENTLEMEN

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According to the arrangement between PCIRI, Changzhou, China and the Wegscheider Farben Ges.m.b.H. & CO KG, Linz, Austria dd 23.11.1990, the above mentioned gentlemen came for training on 4. May 1991 to Linz.

1. RAW MATERIALS

Discussing the raw materials necessary for the production of emulsion-polymerisates and dispersion coatings. In this group are the following products:

- a) insulation primers, knifing putties, dispersion coatings in various qualities for inside, dispersion gloss coatings, dispersion structure pastes, dispersion gloss plastics, dispersion rough-fibre wall-paper pastes, odourless dispersion coatings
- b) dispersion coatings for outside, rubbing plaster in the various grain sizes
- c) wall coatings for inside and outside containing solvents. The gentlemen to be trained brought along raw materials from China, which were compared during the training with the raw materials used in Europe. The testing methods were theoretically explained and practical tests were carried out.

If looking at the wall coating based on dispersions and solvents, these are produced of the following product groups:

.../2

2/31

A) BINDING AGENTS:

These are:

- homopolymer polyvinylacetate dispersions, plastified
 - copolymer polyvinylacetate dispersions of the various monomers
 - terpolymer polyvinylacetate dispersions
 - acrylstyrol dispersions
- dispersions based on
- vinylpropionate
 - vinylacetate-vinylaurate
 - pure acrylates of various alkylmonomers
 - styrol-butadien monomers
 - monomers polymerized under pressure, e.g. vinylacetate/ethylene, vinylacetate/vinylchloride.

The various products were discussed, their application and what care has to be taken, furthermore how these products are tested.

The polymerisates (binding agents) can be tested on the following values:

- a) testing of the solid content
- b) testing of the viscosity
- c) testing of the thixotropy
- d) testing of the white point (film forming temperature)
- e) testing of the alkali-resistance
- f) testing of the water-resistance

B) PIGMENTS:

Dispersion coatings used mainly outside, must be light-fast thus this fact be particularly considered.

The main pigments are

- titaniumdioxide Rutil or Anatas
- iron-oxyd-red, -yellow, -brown, -black as well as some other inorganic pigments as well as a big palette of organic pigments.

To obtain homogenous products, it is necessary, to test these pigments on its' colour intensity.

From this paint pigment (except titaniumdioxide) a paint paste is made and to this a standard paint, in the colour shade white, to an extent of 1 %, 3 % and 5 % is added. One compares either with the eye or with a paint computer the change. In this way the colour intensity can be tested.

However, the pigments must also be tested on light-fastness. Here are various testing methods, the simplest one is the method with the wool-scale. This has 8 light-grades: 8 = very good light-fastness

1 = very bad light-fastness

By dispersion coatings, which particularly are used for outside, the light-fastness must be between 7 - 8.

By interior coatings the light-fastness 5 - 6 can be accepted.

The test results were discussed how the pigments can be compared with the wool-scale. The test is carried out as follows:

From the pigments paint pastes are produced and from this a paint.

This is applied on an underground. The threads of the wool-scale 1 - 8 are taken and bonded on the same underground. One part of the paint and the wool-thread is covered and exposed to uv-light (Hg-light).

After a certain time the colour change is tested by coating and by the wool-thread and determined, which light-fastness the product has.

If by the colour, compared to the wool-thread, by a light-fastness of 7 there is no colour change, then the paint has a light-fastness of 7.

C) FILLERS:

The main fillers used in dispersion paints are:

Calcit 5 and 15 micron - here is meant crystalline calciumcarbonate

Dolomit-powder

Mica (micaceous)

barium sulphate

talkum

kaolin

amorphous calciumcarbonate (chalk)

There are many other fillers and therefore it must be tested which ones are available in the country.

The fillers mentioned here are used in various dispersion coatings, whereby the following tests must be carried out:

1. grading-curve - this must be well-balanced and it should not be a single-grain product.
2. grade of brightness - this can be measured with colour computer or putting the comparative fillers on a glasspane and beside it the filler to be tested. It is covered with a glasspane and tested whether the fillers have the same brightness or whether there are colour differences.

3. alkalinity of the filler - if possible no free CaO should be in the fillers, and if this is the case it must be very little so as not to affect the pH-value of the dispersion paint.

Dispersion paints based on vinylacetate monomer and their copolymer are generally acidic. If alkaline fillers but also pigments are added the pH-value should not reach 7 or lie in alkaline region as then under circumstances it can come to a saponification of the binding agent.

Special fillers in thermo-insulation coatings on solvent-base or in dispersion paints

Dispersion paints can be based on vinylacetate monomer, copolymer, acryl-styrol, as well as on alkydemulsions. Solvent-coatings based on acryl-styrol resins but also based on special alkyd resins.

To increase the thermo-insulation and to decrease the specific weight, but also to increase the vapour permeability, especially by alkyd coatings the following fillers are additionally used:

Celite - filler based on siliciumdioxyd and aluminiumoxyd

Perlit - filler based on aluminiumoxyd, siliciumoxyd, magnesiumoxyd and calciumoxyd

Celite is supplied by M/S Lehmann & Voss, Hamburg, Germany

Perlit is supplied by M/S Deutsche Perlite Ges.m.b.H., Dortmund, Germany

Up to the years 1980 big quantities of special alkyd coatings for facade- but also for interior coatings were used in the USA as well as in Europe. For this reason a soya oil alkyd with an oil-length of 65 %, with siccatives, anti-skin agents and fillers, were used. These products have little importance nowadays because comparing the prices of the copolymer polyvinylacetate dispersion coatings and acrylate coatings, but also the solvent-systems based on acryl-styrol are lower and also because these coatings are often glossy, which nowadays is no more required.

Wall coatings based on soya oil alkyds have been produced for nearly 4 decades and their quality can be counted as good. It has to be noted, however, that these are not alkyd emulsions but alkyd solvent systems. The alkyd emulsion systems were on the world market for a short time only and are hardly produced anymore.

D) WATER:

Water is the only solvent. It must be checked whether the water is free of bacteria.

The hardness of the water is not important by standard products, only by dispersions used for paper lacquers or paper adhesives, the hardness is important. The test on the content of bacteria must be carried out bacteriologically. A simple test can be made as follows:

A potassium permanganate solution is made and the discolouring is tested. If a lot of permanganate is used, the water is not suitable for the production. Of course is the use of demineralized water preferable. Such a high-grade water must not be used for the production of standard dispersions.

E) ADDITIVES:

1. Fungicide

Here 2 types of fungicides can be differentiated:

- a) a fungicide for the preservation of the colour in the tin
- b) a fungicide for the protection of the film and fungal attack or spores.

These fungicides are used as solution with slight quantities of binding agents, to repair walls affected with fungus or to seal them prior to coating, if a higher fungal attack is to be expected. It must be noted that particular this product is of great importance, as the mould fungus decrease the quality and particularly the health of the children can be affected. Therefore it is not allowed to use toxic fungicides like pentachlorophenol-modifications, mercury or tin-compounds.

2. Anti-foam agents

The use of anti-foam agent is absolutely necessary. If foam is in the paint it will very often remain in the film in form of bubbles. These are then defects because here the film will sooner or later tear. Paints containing such bubbles resp. foam, are, however, also much more difficult to process.

3. Dispersing agents

Also dispersing agents are of great importance, as through their use pigments and fillers are better distributed and the content of expensive pigments can be reduced.

Dispersing agents also have a particular influence on the storage stability.

4. Thickening agents

The main ones are acrylate resins, carboxymethylcellulose, methylcellulose, hydroxyethylcellulose, hydroxyisopropylcellulose, starch as well as inorganic thickening agents like colloidal silicic acid, Hektorit (an impure Bentonit).

The Products Hektorit, Bentonit and starch have no significance by coatings, but by adhesives.

The worst thickening agent is carboxymethylcellulose, the best hydroxyisopropylcellulose, the most significant one hydroxyethylcellulose.

These thickening agents do not only have the task to thicken a dispersion coat but to improve the blend and spreadability.

A great disadvantage of carboxymethylcellulose is that mostly it contains salts (sodium chlorid). For the production of high-grade coatings should therefore only be used hydroxyethylcellulose or hydroxypropylcellulose.

5. Special products

These are solvents which improve the white point or the spreadability but also make the film more elastic.

To these products can be counted glycolacidbutylester, ethylenglycolacetate, dibutylphthalate, turpentine, white spirit,...

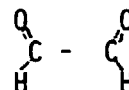
6. Extraordinary products

a) aluminiumsilicate - is an interemediate between pigment and filler, by dispersion coatings e.g. 8 % of the titaniumdioxide can be reduced and exchanged through cheap aluminiumsilicate without diminishing the hiding power. Also the other characteristics do not change. As aluminiumsilicate only costs 1/3 of titaniumdioxid, a lot of money can be saved.

By titaniumdioxide only one Rutil-type can be used. Also in interior areas only Rutil and not Anatas should be used, as in window areas (where it is light) the coat can start to get chalky.

The weather-resistance of the pigments is tested in the weather-o-meter although this does not achieve 100 % values. Therefore it is necessary to make test-panels and these have to be exposed to the various climatic and altitudinal area: sea-, industry-region, mountain-region (3000 m high). These test-panels show whether a paint is weather-resistant.

To increase the water-resistance by dispersions it can have polyvinyl-alcohol as protective colloid (emulgator), $K_2Cr_2O_7$ or glyoxal can be used.



The following must be taken care of.

Potassium-chromate is not suitable because of its' discolouring to yellow-orange. Only glyoxal is suitable. Glyoxal has its effect only when the dispersion is in the acid region, when the pH-value lies below 6. These chemicals are hardly used in paints, generally, however, by adhesives.

2. TESTING OF THE FINAL PRODUCTS AND THEIR PRODUCTION

Dispersion products are principally produced according to the same methods indifferent which products they are.

In a stirrer first the required quantity of water is poured in. This can be done volumetrically, but also through a counter.

Into the water first the additives like fungicides, bactericides, dispersing agents and a part of the anti-foam agents (1/2 the quantity) are added.

After a stirring time of 1 to 2 minutes the addition of the thickening agent is effected. Care has to be taken that the water is not too hot but at a maximum 30 - 35°C. The thickening agent is stirred some minutes until everything is distributed (2-3 minutes). If the temperature is too high it would come to agglomerates which would be difficult to dissolve.

Now are added the alkaline products like ammonia or a NaOH-solution, generally 20%. In a few minutes the thickening agent is dissolved. As thickening agent generally methylcellulose or hydroxyethylcellulose is used. When using other thickening agents, another process can be chosen. Into this thick solution, first the pigments and then the fillers are added. Everything is stirred until the surface is smooth. This is a very easy sign whether the pigments and fillers are completely dispersed.

Now the other additives, e.g. products to decrease the white point, solvents, plasticizing agents are added, ..

The stirring speed when adding the pigments should be relatively high (1000 to 1200 r.p.m.).

Now is added the dispersion, whereby the stirring speed should be reduced to 400 - 500 r.p.m. At the same time is added the rest of the anti-foam agent (second half).

The complete stirring time will be approx. 30 minutes. Now is the testing of the product.

Which tests are carried out?

1. viscosity
2. thixotropy
3. grain fineness
4. hiding power
5. colour exactness

If the tests result in the required values, the product is filled-up.

In case of rubbing plaster, it will be tested whether the product can be rubbed properly. If it seems that the product runs off, further tests will be carried out, which consequently will be discussed.

Principally with dispersions also the following tests can be carried out.

- testing of the alkali-resistance
- testing of the wipe-, wet-wipe- and tack-resistance.

The type of tests are determined through norms which were handed over to the gentlemen.

Additionally can be tested:

1. Behaviour of the product by run-off. On a panel, which has already been sealed with an insulation primer or plaster hardner, in the centre an adhesive tape is bonded. Then the paint or the rubbing plaster is applied on the above area of the panel, i.e. that the product is applied up to the edge of the adhesive tape. The adhesive tape is pulled off and it is tested whether the product runs off.

This test is particularly important by rubbing plaster, because if a rubbing plaster runs off it does not look well optically.

2. Tendency to yellowing

The yellowing of dispersion paints can have its' cause in the use of certain plasticizer, e.g. trikresylphosphate or catalysts existing from the dispersion. There are many catalysts which are used by the polymerisation like cobaltsalts, ironsalts,.. and these can lead to yellowing.

Also through contaminations of the monomers it can come to yellowing.

For this reason the paint-film is applied, half of the coating is covered and exposed to uv-rays. It is tested whether it comes to a yellowing.

3. Storage stability

Deficient storage stability can be seen when a dispersion paint separates water on the surface. The cause is usually in the use of unstable dispersions. The storage stability can be very badly tested. Generally a test is carried out as follows:

The dispersion is stirred 15 minutes with high speed (2000 - 3000 r.p.m.)

A dissolver disc is used.

After a certain storage time it can be seen whether

- a) it comes to water separation and whether
- b) the viscosity and the thixotropy decreases.

This test, however, is a very deficient one and serves only for comparisons.

4. Weather-resistance

This can be tested in a weather-o-meter or in a Florida-Test-Device.

These tests are not 100 %. A real test is the reality. Panels are to be prepared, exposed to weather and continuously controlled. Care has to be taken that these panels are exposed on various places.

These panels should be exposed in moist climate (sea-climate), height (mountains at least 3000 m high), in areas with high sun-rays, by normal climate and in industrial areas.

Only by silicate paints, which also have a certain part of dispersions (mostly acrylstyrol dispersions), is beside the standard test, a further test carried out.

5. On a panel standing at 60° alternatively distilled and undistilled water is poured on it. If the product shows defects, it will come to an opaqueness on the surface, i.e. one will have the impression that the surface is milky. The silicate paint should be tested only after 1 week at the earliest. The panel is laid 60° and water is poured on it from a height of 30 cm. After 4 hours the panel is taken away, dried by room temperature, put back into the device and with the same method treated with distilled water.

This test is carried out 10 days. If the panel is okay after 10 days, can be surely said that the coatings will make no problems.

There are many other tests possible, which in reality are not significant. The testing of the colour-resistance has already been treated.

3. APPLICATION OF THE DISPERSION PAINTS

By the application there are few criteria which could lead to defects.

A dispersion coat or plaster should be applied as follows:

The underground should not be sandy and must be free of lime- and Kaolin-coats. Also it must be free of mould fungus and spores.

If it is a fresh coat, the plaster should at least be 28 days old. If on a fresh plaster the product is applied, it can come to a saponification of the binding agent, especially if not applying acrylates and acryl dispersions.

The affect of mould fungus and spores one can see optically. If these exist a restoration must be started and applied once and if the affect is extreme twice. The interval between these coats should be 24 hours. If on the underground there is lime- or Kaolin-coats, this must be removed, as the adhesion of the dispersion coat would not be enough. The dispersion coat cannot permeate into the underground. The dispersion coat gets tense and tears from the underground with a part of the Kaolin resp. lime-coat. If these conditions are fulfilled it will never come to problems.

However, there is a processing problem as a dispersion coat should only be applied 28 days after a fresh plaster. This period can be shortened to approx. 1 week to 10 days if applying a plaster hardener resp. an insulation primer. The insulation primer is a dispersion, the plaster hardener is an acrylstyrol resin dissolved in organic solvents.

Both products permeate deeply into the underground and enable a consequent and better anchorage and a protection against saponification which exists in the underground.

In reality each dispersion coat should be applied on an insulation primer or plaster hardener.

An advantage when using this product is that much less paint is needed. By interior and exterior coatings a double application is required, only by plasters 1 coat is enough. The consumption for interior use is by 250 - 300 g paint/m², for exterior use by 500 - 600 g/m², by plasters according to roll-grain 3 - 5 kg/m².

Particularly has to be noted that the processing temperature, especially by dispersion is not below +5°C.

If solvent-systems, i.e. products based on acrylstyrol resins, dissolved in organic solvents, are used, no application of a plaster hardener is necessary as this product is absolutely alkaline-resistant, the processing can be effected up to 0°C. This material can also be applied on a plaster being 7 days old and it is recommendable if the plaster has a certain moisture as the product contains components which react with the moisture, thus leading to an even better adhesive power.

The processing of a rubbing plaster causes often problems, particularly when the second rubbing path joins the first path. Here problems by the overlapping, i.e. by the application, can arise.

Thus it depends on the quality of the dispersion and the auxiliaries whether the open time is so long that it does not come to these difficulties.

Coatings containing solvents as aforementioned one will use in industrial-sea-regions but also in foodstuffs-industries by which an intensive cleaning every day is necessary.

4. DISPERSION

From the enclosed tables you can see the dispersions which we produce. The tables are in German language but easy to understand.

The dispersions with the marks 0 - 100 are homopolymer dispersions, whereby the products WEGOPAS D 30 and D 80 are fine-dispers, WEGOPAS D 40 coarse-dispers and WEGOPAS D 60 medium-dispers. All products with a fraction stroke i.e. the number after the fraction stroke shows the part of plasticizer in the dispersion in respect to the solid content, e.g. by WEGOPAS D 30/20, WEGOPAS D 60/25, WEGOPAS D 80/20. By a 50 % dispersion the PVA-part is 37,5 % and the dibutylphthalate part 12,5 %.

Exceptions are WEGOPAS D 63/F - also here the plasticizer-part is 25 % in respect of the solid content, however a fungicide has been polymerized.

By WEGOPAS D 40/50 the number 50 shows only the solid content, also by WEGOPAS D 40/60, 60 is the solid content.

WEGOPAS D 40/60 FH is a plasticized type with 60 % solid content.

Unfortunately these names still exist from the past and we cannot change them yet.

WEGOPAS D 100 - D 300 are copolymer resp. terpolymer dispersions. Also here you can see the solid content and the base.

VAC means vinylacetate monomer

DBM = dibutylmaleinate

Acryl = Acrylate, whereby is not mentioned which acrylate it is

The types 300 - 370 are acrylate-copolymer, whereby WEGOPAS D 333 is a type, which worldwide are only produced by 2 companies. This is an acrylnitril containing tape, which is particularly used by the PVC-bonding.

WEGOPAS D 600 is an acrylstyrol type.

We think that for the begin this survey is enough.

5. TESTING OF THE MONOMERS

The monomers are tested as follows:

1. refractive index (refractometer-value)
2. density

3. optical appearance (paint)
4. boiling analysis
5. water content

Testing of the emulgators

By polyvinylalcohol the viscosity is tested

A 10 % solution is made, this rests and after 1 week the solution is tested a second time. In case the polyvinylalcohol has bubbles, some drops anti-foam agent are added. The polyvinylalcohol solution should rest 6 months and should not discolour.

By hydroxyethylcellulose also the viscosity is tested, namely mostly with a 3 % solution.

Also here the viscosity is tested immediately, after 1 day and after 1 month. In case the product forms bubbles, some drops of anti-foam agents are to be added.

The surface-active substances are not tested, as these are special products for which there are no test-specifications resp. from the companies none are made available.

Testing of the catalysts

The catalysts are partly chemical substances like potassium-persulphate or ammonium, organic or inorganic peroxyds, etc. Here are exact specifications which can be tested.

By the other substances for the REDOX-System no tests are carried out.

Polymerization

There are 3 standard polymerization methods:

the oxidation-method

the REDOX-method

the prepolymer-method

The gentlemen were shown all polymerization methods, whereby the polymerization partly was carried out with Chinese raw materials.

Significant for the polymerization is that the hydroquinone is removed from the monomers. The removal can be effected:

- a) through distillation
- b) through washing out with NaOH-solution
- c) through the use of bigger quantities catalysts.

Only the distillation-method is practical and obtains final products of high quality.

Only our company knows a method by which the hydroquinone is blocked. The method is very cheap and reduces the production costs for about 50 %. The method is applicable on every plant.

The polymerization plant with prepolymer-method is somewhat different than by the oxidation- and REDOX-method. The emulgator boiler must be at least 70 % of the polymerization boiler, whereas by the oxidation- and REDOX-method it makes generally 50 %.

The aforementioned polymerization-methods are pressureless. Copolymers based on vinylacetate/ethylene and vinylacetate/vinylchloride are polymerized under pressure. This method was not explained.

The emulsion-polymerization generally is exothermic, therefore the reaction-temperature is regulated through the feed speed of the monomers. If energy must be let in, this shows that the polymerization does not work properly. Generally the polymerization can be described as follows:

The emulgator solution is produced in the emulgator boiler, whereby it is important that the finished emulgator solution e.g. polyvinylalcohol or hydroxyethylcellulose rests 1-2 hours before using it by the polymerization. It can be seen that emulgator solutions which are used immediately, do not bring forth such good final products. The emulgator is produced as follows: Water is pumped into the boiler, the water temperature should not exceed 30°C. Then is added the emulgator resp. the protective colloid like hydroxyethylcellulose, polyvinylalcohol, but also surface-active substances, heat up to 90°C whereby stirring at the same time. This process lasts approx. 2-3 hours.

Then the solution rests.

This solution is pumped into the reactor, then is added a part of the catalysts as well as other products and a part of the monomers. The temperature rises to polymerization temperature. This temperature is regulated through continuous feed of the oxidation- and reduction-solution, resp. only the oxidation solution and the monomers.

After the complete quantity of monomers has been fed a small quantity of oxidation- or oxidation- and reduction-solution will be added. The content of free monomer should not be higher than 0,1 %.

By the polymerization other additives like chain-controls, fungicides, stabilizers, anti-foam agents, .. are added.

The gentlemen were trained in the laboratory as well as on a big polymerization plant, whereby they could follow the polymerization process very detailed.

The polymerisates were then tested on:

1. viscosity
2. thixotropy
3. density
4. film characteristics
5. water resistance of the film

Comprising can be said that a complete training in the polymerization is only possible when all secrets of the polymerization are revealed. This is particularly the case on the type of catalysts, emulgators and additives.