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D'importantes étapes ont été réalisées ces dernières années pour améliorer la qualité des miroirs, non seulement du point de vue du dépôt de peinture mais aussi dans le procédé chimique permettant la production des miroirs. Ce nouveau process a permis de développer des systèmes de peinture avec des teneurs en plomb faibles voire nulles tout en maintenant ou en augmentant les propriétés du miroir. Cette étape a permis de rendre les produits plus respectueux de l'environnement. Les développements actuels portent sur la réduction des COV, en évitant les substances dangereuses comme le formaldéhyde par exemple, etc. Sur le marché, il est possible de trouver des systèmes à base de solvant. Aujourd'hui, des systèmes aqueux sont prêts à être commercialisés. Ce document donne un aperçu des différents produits disponibles.

Future of mirror paints

Some important steps have been done in the last years to improve the quality of the mirrors, not only from a paint point of view but also in the chemical process to produce mirrors (Cu-free process). The new process allowed to develop paint systems with a low or even zero lead content maintaining or even improving the overall properties of the mirror. This was a good step to make the products more environmental friendly. New developments are actually mainly based on further reducing VOC avoiding dangerous materials (like formaldehyde) etc. On the market you will already find high solid (solvent based) systems but also water based systems are ready to be introduced in the market. An overview.

With the authorization of the author Piet De Vos
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INTRODUCTION

During the Greek and Roman empires, mirrors were nothing more then well polished metal plates made out of tin, silver or bronze. In the Middle Ages, the first mirrors based on glass with a metallic layer were produced; Venice and Nürnberg were the centers of mirror production. Mirrors were at that time made of liquid metals (amalgam with tin and mercury). No need to say that producing these mirrors was very unhealthy but the properties were acceptable at that time.

In the 19th century, silver mirrors were invented with a layer of cupper to protect the silver layer. Lead containing paints were used to protect this Ag/Cu layer. At the end of the 20th century a passivation layer was used to eliminate the cupper layer (Cu-free process).

PAINT SYSTEMS FOR SILVER/COPPER MIRRORS

The production of Ag/Cu mirrors started at the end of the 19th century or beginning of the 20th century and is up to now still used. The process consists out of the following:

1) Cleaning & polishing of the glass
2) Activation of the glass
3) Silvering (reduction of $AgNO_3$ to metallic Ag)
4) Coppering (reduction of $CuSO_4$ to metallic Cu)
5) First paint (base coat)
6) Second paint (topcoat)
7) The paint systems currently used are single or double coat systems.

Typical properties of single coat systems:

- Contains anti corrosion lead pigments (2 – 8 %)
- Based on synthetic resin systems
- Solvent based
- Show good corrosion in CASS, Salt spray and humidity tests
- Good physical properties: adhesion, hardness...

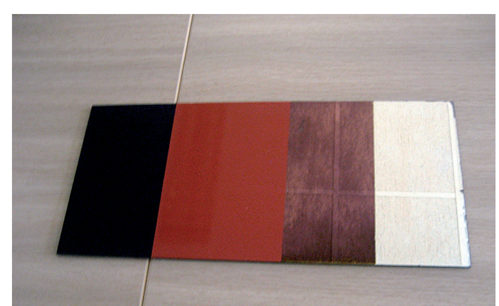

Figure 1. Classical Ag/Cu mirror with 2-coat system

Typical properties of a double coat system:

- Contains anti corrosion lead pigments (basecoat). Lead pigments can be avoided in topcoat.
- Based on synthetic resin systems
- Solvent based
- Show good corrosion in CASS, salt spray and humidity tests
- The base coat is designed to give good corrosion properties to the

mirror to avoid black spots or corrosion at the borders. The topcoat gives mechanical and chemical protection to the mirror.

Developments for silver/copper mirrors:
– Waterbased systems can be used for single coat and the topcoat of a double coat system.
– Avoiding anti corrosion lead pigments is difficult and will make the mirror less corrosion resistant.
– Lead containing water based systems exist but requires an adequate conveyor line.

PAINT SYSTEMS FOR COPPER-FREE MIRRORS

At the end of the 90s a new technology was introduced and this was a break through on the road to produce more environmental mirrors: copper-free.
The process consists out of the following:
1) Cleaning & polishing of the glass
2) Activation of the glass
3) Silvering (Reduction of $AgNO_3$ to metallic Ag)
4) Passivation treatment
5) Coating preparation
6) First paint (base coat)
7) Second paint (topcoat)
The paint systems currently used are single or double coat systems.

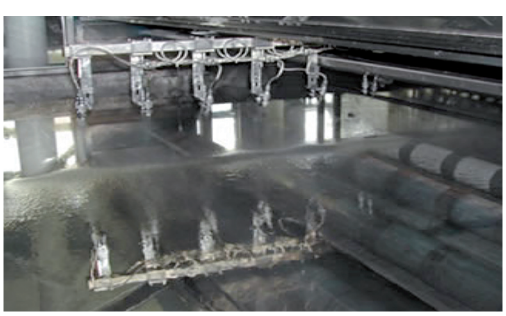

Figure 2. Application of the Ag to the glass

Typical properties of single coat systems (compared to silver/copper mirrors):
– Possibility to avoid lead anti corrosive pigments (version with lead still exists)
– Based on synthetic resin systems
– Solvent based
– Show good corrosion in CASS-test, Salt spray: about 200 % less corrosion compared to Ag/Cu mirrors
– Good physical properties: adhesion, hardness…

Typical properties of a double coat system:
– Possibility to avoid lead anti corrosive pigments (basecoat). No lead pigments in topcoat.
– Based on synthetic resin systems
– Solvent Based
– Show good corrosion in CASS-test, Salt spray: about 200 % less corrosion compared to Ag/Cu mirrors
– The base coat is designed to give good corrosion properties to the mirror to avoid black spots or corrosion at the borders. The topcoat gives mechanical and chemical protection to the mirror.

Developments for copper-free mirrors:
– Water based systems exist for single coat and the topcoat of a double coat system
– Completely lead-free (0 % Pb) or low lead systems (< 0.5 % Pb) exist and give similar results compared to lead containing paints.

FUTURE CHALLENGES

In a world were quite a lot of solvent based paints have been replaced by water based systems (e.g. Decorative paints, DIY, automotive paints…) we still see that practically all mirror producers around the world still use solvent based (aromatic, esters) paints. Some developments have been done by using high solid systems hence lowering the solvent content to a level of about 10-15 % by weight. A further reduction of solvents is possible by using low molecular resin systems that have a low viscosity at application. Also as already mentioned water based systems exists but require also changes of production lines to prevent them from corrosion as most lines are made out of steel and this should be replaced by stainless steel. Other systems like UV curable systems have been under development but are economically not feasible.
Currently with the copper-free process it is possible to use lead-free paints which give good results. Some businesses like automotive or electronics already require the use of almost lead free paints for mirrors to be RoHS compliant (< 0.1 %). In general the use of dangerous materials like lead pigments have to be avoided for environmental reasons but in most countries there is still no legislation.
Melamine resins are used in most mirror paints. These melamine resins contain in most cases also formaldehyde which is a toxic material which is even in some countries forbidden to be used.
Some alternative systems have been developed to avoid the use of melamine resins and hence to avoid formaldehyde. These systems are mostly based on epoxy resin systems and are now starting to be used in the market.
During 2008 the world was confronted with high crude oil prices and high energy costs. Also it is clear that the world has to look for environmental friendly energy sources as these fossil fuels will not be endlessly available. One of the possibilities is concentrating solar light to 1 single point by the use of mirrors. This can be done in different ways but as mirrors are traditionally used inside, we now have to develop mirrors that will be used outside in severe conditions and the paint used will play an important role.

PAINT SYSTEMS FOR SOLAR MIRROR APPLICATIONS

Most of the mirrors produced these days are mainly used for indoor applications.
The demand for mirrors for solar applications is growing more and more and these mirrors are exposed outside in an aggressive

environment (high UV-exposure, very dry or humid environment, sand storms....) and hence some quality specifications have to be adapted or added.

Standard tests for mirrors include (according to EN 1036):
– CASS-test according to EN-9227 (120 h): < 2,5 mm edge corrosion
– Salt spray-test according to EN-9227 (480 h): < 1.5 mm edge corrosion
– Humidity resistance (40° C - 100 % relative humidity): < 0.2 mm edge corrosion, no blistering.

Figure 3. CASS and salt spray testing equipment

Special tests for testing solar mirrors for outdoor durability:
– Climatic cycle test according to EN-1279-2
– QUV test (UV resistance)
– Weatherometer WOM
– Sand abresion test according to ASTM D968.

Figure 4. QUV testing equipment

The special tests are intended to test the outdoor durability of the mirrors. Of course it is always difficult to predict real life situations with these accelerated tests. We believe we can relate these results to an outdoor exposure of 15-20 years with a loss of reflectivity of max.1 %.
Paint systems that can be used for solar mirror applications:
1) Three Coat system:
– 1st layer: base coat with/without lead for the chemical protection of the metal layers
– 2nd layer: Intermediate coat without lead
– 3rd layer: Topcoat with UV absorbers and high mechanical resistance.
Average recommended paint thickness should be about 25 μ for all layers.

2) Two Coat system:
– 1st layer: base coat with/without lead for the chemical protection of the metal layers
– 2nd layer: Topcoat with UV absorbers and high mechanical resistance.
Average recommend paint thickness is 25 μ for basecoat and 35 μ for topcoat.

The following results can be achieved:
Three Coat system:
– CASS-test (EN-9227): corrosion < 200 μ (120 h) or < 500 μ (480 h), loss of reflectivity < 1 %
– Salt spray -test (EN-9227): corrosion < 50 μ (480 h), loss of reflectivity < 1 %
– Humidity test (40 °C/100 % RH): corrosion < 50 μ, some blisters, loss of reflectivity < 1 %
– Climatic cycle test (EN-1279-2): corrosion < 100 μ, loss of reflectivity < 1 %
– QUV test (3000 h): corrosion < 50 μ, no delamination, loss of reflectivity < 1 %
– Weatherometer WOM (3000 h): corrosion < 50 μ, no delamination, loss of reflectivity < 1 %
– Sand abrasion (ASTM D968): 300 g- 400 g/μ

b) Two Coat system:
– CASS-test (EN-9227): corrosion < 200 μ (120 h) or < 500 μ (480 h), loss of reflectivity < 1 %
– Salt spray -test (EN-9227): corrosion < 50 μ (480 h), loss of reflectivity < 1 %
– Humidity test (40 °C/100 % RH): corrosion < 50 μ, some blisters, loss of reflectivity < 1 %
– Climatic cycle test (EN-1279-2): corrosion < 100 μ, loss of reflectivity < 1 %
– QUV test (3000 h): corrosion < 50 μ, no delamination
- Loss of reflectivity depends on paint thickness: > 60 μ gives < 1 % loss
– Weatherometer WOM (3000 h): corrosion < 50 μ, no delamination, loss of reflectivity < 1 %
– Loss of reflectivity depends on paint thickness: > 60 μ gives < 1 % loss
– Sand abrasion (ASTM D968): 250 g- 300 g/μ

Figure 5. Solar mirrors in the desert

CONCLUSIONS

Some big steps have already been made to produce better mirrors which are becoming more and more environmental friendly by reducing the lead content, VOC etc.
Some technologies like water based products are ready and will be introduced in the market soon. Developments have been done to make mirror paints systems that can be used for outdoor solar power stations, further developments are still running to further improve the resistance.
The final properties of these solar mirrors are of course not only depending on the paint systems used but also on other factors like the silver and copper layers, production process and installation of the mirrors. ■