Special aluminum pigments in the packaging and label market.
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A new class of high brilliant mirror effect inks is now able to provide a realistic alternative to foil blocking, cold foil, and metalised substrates with economic advantages in both product cost, and in some cases by removing the need for costly and time consuming offline downstream operations following printing. This new ink concept allows any printer using one of the offset, flexo, gravure or screen-printing process methods to take advantage of their use on press.

The basis for these innovative inks are special aluminum pigments which are manufactured in a typical PVD (Physical Vapor Deposition) process and thus provide a metallic effect which is far beyond what is known from conventional metallic pigments produced from atomized metallic powder.

Manufacturing process for PVD-aluminum pigments
In a discontinuous process, a release coating (typical resin systems used are acrylics, cellulose systems, vinyl resins etc.) is applied to at least on side of a carrier sheet by a coating or printing technique (preferably rotogravure or flexo). Suitable carriers are films consisting of polyesters, polyolefins or other common materials.

The coated film is then passed through a roll coater where a very thin aluminum layer is deposited on the release-coat in a typical PVD (Physical Vapor Deposition) process.

The thickness of the deposited aluminum is critical to obtain the desired properties of the final pigments. Usually, the thickness is adjusted between 30 and 50nm. At a thickness above 50nm the orientation ability of the pigments is negatively influenced and the scattering effects at the edges of the pigments increase. Both effects have a negative impact on brilliance, opacity and flop.

At a thickness below 30nm the aluminum becomes transparent and handling of the pigments is more difficult due to higher agglomeration tendencies.

In the next step the metallised film runs through a solvent tank (stripper) were the release coat is dissolved and the aluminum layer is removed as fragments or coarse flakes. The aluminum fragments or coarse particles are washed and concentrated if desired to a dispersion normally containing 10 to 20% pigment. The particles are then sized by vigorous stirring or ultrasonic treatment (Figure 1).

Metallic effect is based on reflection and scattering
To understand the special mirror effects provided by those pigments it is helpful to have a closer look on the principles of the metallic effect, how it is influenced by pigment properties and what the major differences between "conventional" metallic pigments (metallic pigments based on atomized metallic feedstock and milled in ball mills) and PVD-pigments are.

In case of perfectly flat, high gloss surfaces (e.g. mirrors), the law of reflection is valid: angle of illumination = angle of reflection. These types of surfaces are also considered image forming as the image of a reflected object can be distinctly seen. The light is reflected at the first surface into the specular direction of reflection. In case of perfectly dull surfaces, the light is scattered in all directions without a specular reflection.

Metal pigments exhibit a combination of specular reflection arising from the (ideally) flat surface of the pigment and scattering caused by the pigment edges or defects on the pigment surface (Figure 2).

How to maximize reflectance
To optimize the metallic effect it is therefore necessary to maximize the specular reflectance and to minimize the scattering.

Common discussions about pigment parameters which influence the metallic effect and how to improve this effect contain aspects like particle shape (e.g. cornflake vs. silver-dollar), particle size and particle size distribution. Those considerations, however, are not very helpful to describe the difference between conventional flakes and PVD-pigments as they are only valid when flakes which are manufactured according to the same technology are compared (e.g. comparison of fine and coarse particles manufactured in ball mills).

In case of PVD-pigments those parameters are almost irrelevant as particle shape, size and distribution can not be taken to explain the mirror like effect and have by far a smaller impact on the effect.

Instead of this, two other properties are much more important:
- Particle thickness
- Surface topography of the platelets

Smaller thickness - better orientation - more reflectance
As already mentioned the thickness of PVD-pigments as compared to conventional flakes is approx. 5 to 10 times smaller (30 to 50nm vs. 100 to 500nm). This increases the mobility of the pigments significantly and allows them to be scattered in parallel to the surface of the substrate much faster than conventional pigments within a given time frame, e.g. during the short drying process of an ink (Figures 3a and 4a). The final orientation is only influenced by the topography of the substrate, the formulation parameters and the application technique but not limited anymore by the insufficient mobility of the pigment as is sometimes known from conventional flakes.

As demonstrated in Figure 3a, optimized orientation results in improved brilliance, flop and coverage.

In addition, when viewed on top of a typical application with said PVD-pigments with an electron microscope, it is almost impossible to identify the edges of the pigments. Due to the extremely thin particles, the flakes form a nearly uniform surface without many visible edges where the light can be scattered. In comparison, applications with conventional pigments show the contours of each single pigment particle (Figures 3b and 4b).

Figure 3b demonstrates this effect which, in the case of very thin PVD-pigments, ultimately leads to an improved metallic character (high brilliance, good flop and coverage).

Smooth surface topography like micro mirrors
Scattering and disordered reflection of light not only occurs at the pigment edges but also at defects on the pigment surface.

Conventional pigments are exposed to strong mechanical forces during the milling process resulting in uneven flakes with an irregular thickness and a large number of surface defects.

PVD-pigments, however, show a homogenous thickness and hardly any surface defects (Figure 4b) and, therefore, guarantee a high level of specular reflectance. For this reason those pigments are often called micro mirrors.

PVD-pigments fulfill perfect non-leafing property

Micro mirror

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To complete this discussion of PVDA-pigments one further property is worthwhile mentioning: the perfect non-leafing behavior (see Figure 5).

This property is generally known from conventional pigments and therefore not unique to PVDA-pigments. However, this behavior opens up a wide range of formulation and application possibilities. The listed parameters are very closely connected with the manufacturing process of those PVDA-pigments; allowing a defined and controlled adjustment of all relevant physical and chemical properties of the deposited metallic layer and after all securing a unique combination of excellent effects:

- High brilliance
- Hiding power
- Strong flop effect
- Non leafing behavior
- Suitable for tinting
- Rub resistance
- Intercoat adhesion

**PVDA-inks: concepts and properties**

The effects achievable with PVDA-pigments not only depend on the typical pigment properties but are additionally very much influenced by other, non pigment specific, parameters such as ink formulation and application conditions.

The ink formulation as well as the application technique and the quality of the substrate where the ink is printed on must guarantee and support an ideal orientation of the pigments to ensure a high degree of metallic effect, brilliance, opacity and flop.

Ideal parameters are:
- Low viscosity systems
- Low binder contents or high pigment/binder ratios
- Low pigment loading
- Low film thickness
- Smooth and even substrates

Less favorable systems or conditions are therefore formulations with high viscosity or high binder content, applications resulting in high film thickness and applications on uneven or absorbent substrates.

**PVDA-pigments are suitable for most systems**

Due to the required conditions mentioned above, but primarily due to the fact that PVDA-pigments were originally only offered as dispersions in various acetates, the main application in the past was solvent based gravure printing, followed by only a few screen applications (e.g. on compact disks, signs etc.). This limitation completely excluded the offset and primarily the flexo market where suitable inks are water based, alcohols based or UV-curable. Since recently, however, new pigment, additive, ink formulation, and sometimes also with compromises in terms of the resulting quality.

PVDA-inks, however, can be applied in one of the a.m. printing processes only in the areas where it is required. In many cases this results in significant cost savings and faster production.

The final cost comparison between the selective application of PVDA-inks and the above mentioned alternative technologies is primarily only determined by the percentage of metallic coverage on the label or packaging, run length, design and raw material costs.

This calculation may also be different for certain market segments. Typical market segments where this concept is already realized and works in the favor of the printer, designer and brand owner are described in the following.

**Dominating wet glue labels market**

This market is dominated by solvent based gravure printing and consequently was the first market where PVDA-inks were used and successfully gained more and more share vs. metalised paper. This primarily because of the cost savings achievable but also because of advantages in possible recycling processes of the label where metalised paper may cause problems in the de-inking step. Depending on the run length and the raw material costs of the printer, the "break even point", that means the percentage of metallic coverage on the label up to which the use of PVDA-inks is more economic over metalised paper, can be up to 25% or even 30%.

Acetate based PVDA-inks used in this area provide all the necessary properties such as perfect rub resistance, excellent properties in the de-inking and recycling process and also guarantee a wide spectrum of polychromatic colors by simply tinting the ink with transparent color pigments or suitable dyes.

**PVDA-inks replace foil blocking by pressure sensitive labels**

Pressure sensitive labels are primarily narrow web flexo printed with water based or UV-curing inks, but partially also
with alcohol based inks. Typical substrates used are self adhesive paper or film qualities (PET, OPP etc.) but also increasingly PVC-shrink films. Hot foiling is primarily used in order to achieve brilliant metallic effects, however, very often comes along with partially huge wastage of material (depending on percentage metallic coverage on the label) and a decreased printing speed or sometimes offline processes following printing. PVDA-inks are available for all of the mentioned systems used (water-based, alcohol based, UV-curing) and can be selected according to the printing conditions and required surface of the resulting product. Quite recently new press concepts have been introduced which now also enable the narrow web label printer to utilize solvent based gravure printing.

Using PVDA-inks instead of foil blocking can be cost efficient up to a metallic coverage on the label of 25 - 30%, whereas most of the labels do normally not require more than 20% metallic coverage.

Flexible packaging demands a demetalising process
Metalled film is widely used in order to provide a attractive metallic look, but in many cases only in a few areas of the packaging. In other cases it is necessary to demetallise in order to leave a clear window as already described above. In all cases the demetallising process requires additional working steps following printing and is very time and consequently cost consuming. Recently PVDA-inks have started to gain more and more share against metalised substrates where the packaging design demands a demetalling process. Today a wide palette of different PVDA-inks is available for solvent based flexo and gravure printing on different film materials providing excellent adhesion and lamination properties. As already described, the best effects can be achieved by reverse printing, however, even surface printed effects (partially tinted in order to achieve polychromatic colors) can easily provide interesting alternatives. The percentage of required metallic effect on the packaging up to which the use of PVDA-inks is more economic over the demetallising process could be up to 50% or even 60% (depending on run length, raw material costs etc.).

Result at a glance
The ability of PVDA-inks to offer a level of metallic effect and brilliance that is similar to metalled substrates or foil blocking consequently means that the selection of the favored process primarily only depends upon the relative cost balance. Independent of the market segment, the desired substrate and printing process, PVDA-inks can provide cost saving potentials for low to medium percentage of metallic coverage. Keeping in mind that many of the label or packaging designs only require those small areas of metallic effect, PVDA-inks will more and more be considered and used in order to add value to the label or packaging and additionally help the printer or brand owner to do so at lower costs than he was able to do so in the past.

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-> Dr. Jörg Seubert, Echart GmbH&Co. KG, joint in 1995 where he started working in the R&D department for bronze pigments and later in the product development for the Graphic Arts market. Today he is in charge of R&D and technical service Liquid Ink products and the Product Management for PVD-aluminium pigments.

ETAD Award 2004
Call for submissions
Papers on reducing environmental and health impact of organic colorants are solicited to be submitted for the ETAD Award 2004. Innovation plays a major role in reducing the adverse impact of organic colorant products on health or the environment. To encourage these innovation efforts, ETAD, the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers, gives an award of 10,000 CHF to the author of a scientific publication that is of particular relevance to the organic colorants industry in the fields of ecology, toxicology, or analysis. ETAD is now announcing the call for submissions for the ETAD Award 2004. The ETAD Award 2004 will be given to the author of a scientific publication which addresses organic colorant issues. The paper must have been published on or after January 1, 2002, or have been accepted for publication. Submissions must be received by the ETAD Secretariat in Basel, Switzerland, between September 1, 2003, and January 31, 2004. The number of applications is limited to one paper per applicant. A completed entry form, available from the ETAD Secretariat, must be sent with the paper submitted. Papers must be submitted between September 1, 2003, and January 31, 2004 to: ETAD Secretariat, Postfach 99, CH-4005 Basel, Switzerland, Fax +41 61 691 42 78, info@etad.com. The winner will be announced on March 1, 2004. The award ceremony will take place at the ETAD General Assembly meeting on May 13, 2004, near Brussels, Belgium, where the winner will also present his paper.

ETAD was formed in 1974 to represent the interests of the dyes and organic pigments manufacturers on matters relating to the organic colorants industry in the fields of health and environment. ETAD is an international organization with currently 45 member companies from 14 countries. Member companies are obliged to adhere to the ETAD Code of Ethics, which is based on the principles of responsible care. The ETAD Award 2004 is part of the organization's efforts to foster and coordinate the endeavours of its members to minimize any possible adverse impact of organic colorants on health and the environment throughout the chain of manufacture, use, and ultimate disposal. Innovations in this field include the development of new colorants and formulations, as well as new effluent treatment processes and other process improvements.
Figure 1: Manufacturing process for PVDA-pigments
Figure 2: Metallic effect: reflection and scattering
Figure 3: Theoretical approach: particle thickness influence: a) on orientation
Figure 3: Theoretical approach: particle thickness influence: b) on visible pigment edges
Figure 4: SEM-photographs: particle thickness influence: a) on orientation
Figure 4: SEM-photographs: particle thickness influence: b) on visible pigment edges
Figure 5: Leafing and non-leafing behavior

- **Leafing**
  - Poor pigment wetting
  - Orientation at the surface of the coating
  - Poor rub resistance
  - Poor intercoat adhesion

- **Non-leafing**
  - Good pigment wetting
  - Orientation within the coating
  - Excellent rub resistance
  - Excellent intercoat adhesion
  - Ideal for tinting
Figure 6: Gloss of metallic prints with PVDA-inks