Two-way protection

Organic/inorganic hybrid anitcorrosive pigment outperforms zinc phosphate

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Environmental requirements call for the development of more efficient anticorrosive pigments, free of toxic heavy metals. A zinc-free anticorrosion pigemt based on organically treated calcium strontium phosphosilicate with a very fine particle size has been developed on this purpose. This pigment was found to show much better anticorrosive properties than standard zinc phosphate in salt spray tests.

The need for non-toxic products has increased lately, especially in the field of anticorrosive primers and paints, where most pigments have been chromate or lead based compounds. For two decades, zinc phosphate has been the standard non-toxic pigment used instead of chromates. Due to their great efficiency and superior characteristics, modified phosphates chemically treated and with special particle design form the new generation of non-toxic anticorrosive pigments [1].

Nevertheless, environmental requirements mean that pigment producers must advance one step more in finding zinc-free anticorrosive pigments. This new generation is represented by Nubiola's anticorrosive pigment "Nubirox 302", an organophilised calcium strontium phosphosilicate free of zinc and organically treated. This new pigment has been compared to standard zinc phosphate, as described below.

The value of experimental design

Statistically-based design of experiments (DOE) has been described as a powerful formulation tool in coatings [2]. DOE provides validated models including any significant interactions that allow response measures to be confidently predicted as a function of the inputs.

Product	Function	Supplier	Formula 1 (3 % ZnPh) % weight	Formula 2 (6 % ZnPh) % weight	Formula 3 (3 % Zn-free) % weight	Formula 4 (6 % Zn-free) % weight
Millbase						
Water	Solvent		9.71	9.75	9.49	9.33
Byk 154	Dispersing agent	Byk-Chemie	0.57	0.56	0.58	0.59
Surfynol 104 E	Wetting agent	Air Products	0.16	0.15	0.16	0.16
Tioxide TR92	Titanium dioxide	Huntsman	7.56	7.50	7.62	7.63
Zinc Phosphate	Anticorrosive pigment	Nubiola	3.19	6.33	-	-
Nubirox 302	Anticorrosive pigment	Nubiola	-	-	2.84	5.70
Plastorit Micro	Mica/quartz/chlorite filler	Rio Tinto Minerals	14.22	11.82	13.45	10.25
Byk 024	Antifoam	Byk-Chemie	0.07	0.07	0.07	0.07
Nubirox FR-10	Flash-rust inhibitor	Nubiola	0.16	0.15	0.16	0.16
Letdown						
Encor 2401	Styrene-acrylic dispersion	Arkema	60.15	59.42	61.46	62.02
Texanol	Coalescing agent	Eastman	3.64	3.66	3.56	3.50
Acrysol RM2020	PU-thickener	Dow Chemical	0.13	0.13	0.14	0.14
Byk 024	Antifoam	Byk-Chemie	0.32	0.32	0.33	0.33
Ammonia	Neutralising agent		0.12	0.12	0.13	0.13
		Total	**100.00**	**100.00**	**100.00**	**100.00**
Physical properties						
Pigment Volume Concentration [%]	24.3	24.7	23.3	22.7		
PVC/CPVC		0.47	0.47	0.47	0.47	
Non-volatile content, volume [%]	41.0	41.0	41.0	41.0		
Non-volatile content, weight [%]	51.9	52.3	51.4	51.3		
Density (g/ml)	1.21	1.22	1.20	1.20		
VOC [g/l]	< 140	< 140	< 140	< 140		
Anticorrosive pigment volume in dry film [%]	3.0	6.0	3.0	6.0		

Table 1: Formulas of WB styrene-acrylic primer with 3 % and 6 % anti-corrosive pigment

Run	Time [h]	Thickness µm	Dose [%]	Pigment	Adhesion at scribe (ASTM D1654 B-91)	Oxidation at scribe (ASTM D1654 A-91)	Oxidation on panel (ASTM D610-01)
1	240	60	3	Conv. ZnPh	9	5	3
2	240	60	3	Zn-free	10	8	9
3	240	60	6	Conv. ZnPh	9	8	5
4	240	60	6	Zn-free	10	7	10
5	240	90	3	Conv. ZnPh	10	7	5
6	240	90	3	Zn-free	10	9	10
7	240	90	6	Conv. ZnPh	10	8	5
8	240	90	6	Zn-free	10	9	10
9	1170	60	3	Conv. ZnPh	6	4	2
10	1170	60	3	Zn-free	6	6	1
11	1170	60	6	Conv. ZnPh	6	6	2
12	1170	60	6	Zn-free	8	6	4
13	1170	90	3	Conv. ZnPh	6	4	2
14	1170	90	3	Zn-free	9	5	4
15	1170	90	6	Conv. ZnPh	8	5	3
16	1170	90	6	Zn-free	9	7	7

Table 2: Experimental factors and levels

The strategy of DOE is simple: to use screening designs to separate the few most important factors from the trivial many. This is followed by an in-depth investigation of the remaining key factors.
In order to identify trivial factors, responses must be as accurate and reliable as possible. One of the methods is to use replicates to calculate variance and the significance of the different effects. Nevertheless, replication involves more experiments, time and money. An alternative possibility is to use an NPP (Normal Probabilistic Plot) for two-level designs involving two to four factors.

Physical and chemical contributions to protection

The anticorrosive pigment tested is a zinc-free corrosion inhibitor, specifically an organophilised calcium strontium phosphosilicate, with the chemical composition $aM^{*}. bP_2O_5 . cSiO_2 . xH_2O$, which has been designed to give anticorrosive efficiency in a wide variety of paint systems. This pigment shows a high efficiency as a result of its chemical composition and physical characteristics.

Results at a glance

››› Environmental requirements call for the development of more efficient anticorrosive pigments free of toxic heavy metals. A zinc-free anticorrosion pigemt based on organically treated calcium strontium phosphosilicate with a very fine particle size has been developed on this purpose.

››› This pigment shows much better anticorrosion properties than the standard zinc phosphate with which it was compared in salt spray tests. It is more effective than zinc phosphate even at a lower dose and film thickness.

››› Anticorrosive properties can be improved by increasing the thickness of the coating (90 µm) and the dose (6 %).

››› The adhesion at the scribe depends more on the time of exposure to salt spray than on the type of pigment, and for this reason it can be related to cathodic delamination phenomena.

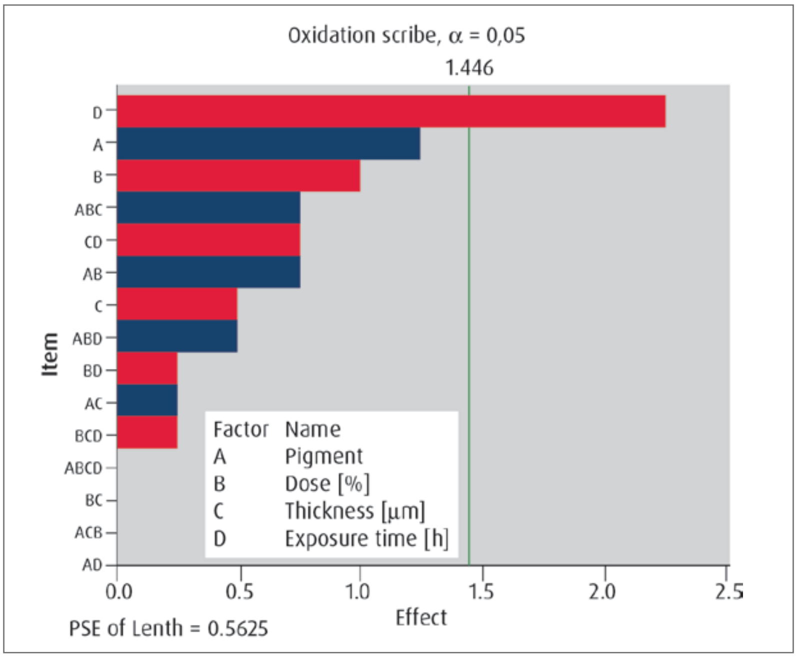

Figure 1: Pareto plot of effects (oxidation at the scribe, α = 0.05, PSE = Pseudo Standard Error)

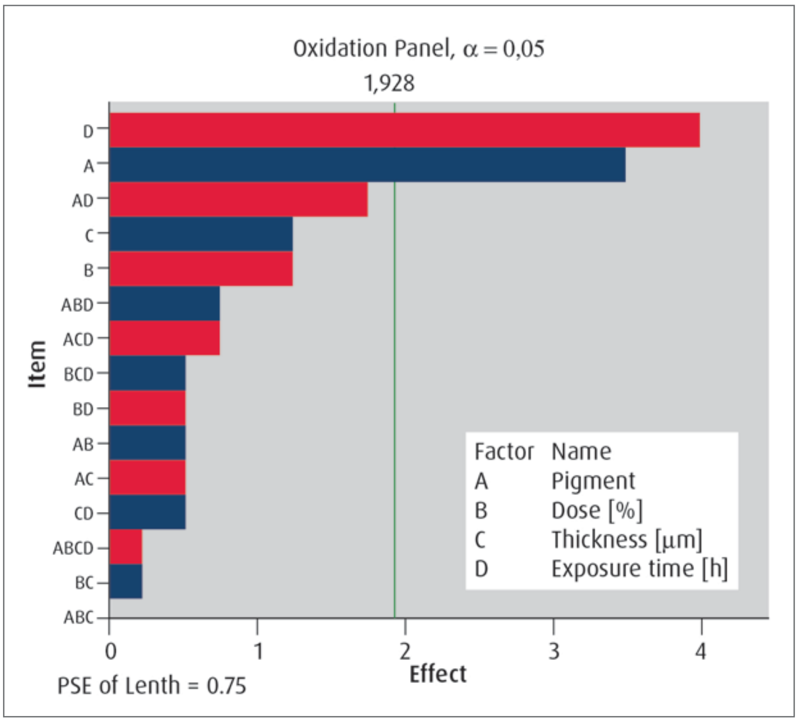

Figure 2: Pareto plot of effects (oxidation on the panel, α = 0.05, PSE = Pseudo Standard Error)

Chemically it consists of inorganic and organic components which show synergistic effects. Its inorganic content works on the anode and the cathode. Specifically, at the anode it passivates with the precipitation of insoluble calcium, strontium and iron phosphate complexes that reduce iron cation migration.
At the cathode it inhibits via the precipitation of calcium and strontium hydroxides that make the passage of oxygen more difficult. In addition, the basic nature of the pigment reduces the amount of oxygen needed to passivate the formation of rust.
Further, its organic surface treatment reduces particle agglomeration; it also improves film formation, promotes adhesion and improves the pigment-binder interface, which makes the flow of water and electrolytes through the organic coating more difficult.
But as already stated, its effective performance depends not only on its chemical composition, but also on its physical characteristics. One of the most significant physical features is its small particle size. These particles also have a special particle size distribution, that shows mean elemental particles around 1 µm and aggregates and agglomerates up to < 10 µm. This distribution has been specially designed to increase the anticorrosive efficiency.
One of the main effects of this small particle size is to provide easier solubility due to its high specific surface value, which is 20 times higher than in standard zinc phosphate, and which is one of the keys to its anticorrosive effectiveness. In addition, the special particle size distribution is also responsible for a lower effect on gloss than zinc phosphate based anticorrosive pigments, which is especially interesting in glossy DTM (Direct to Metal) systems.

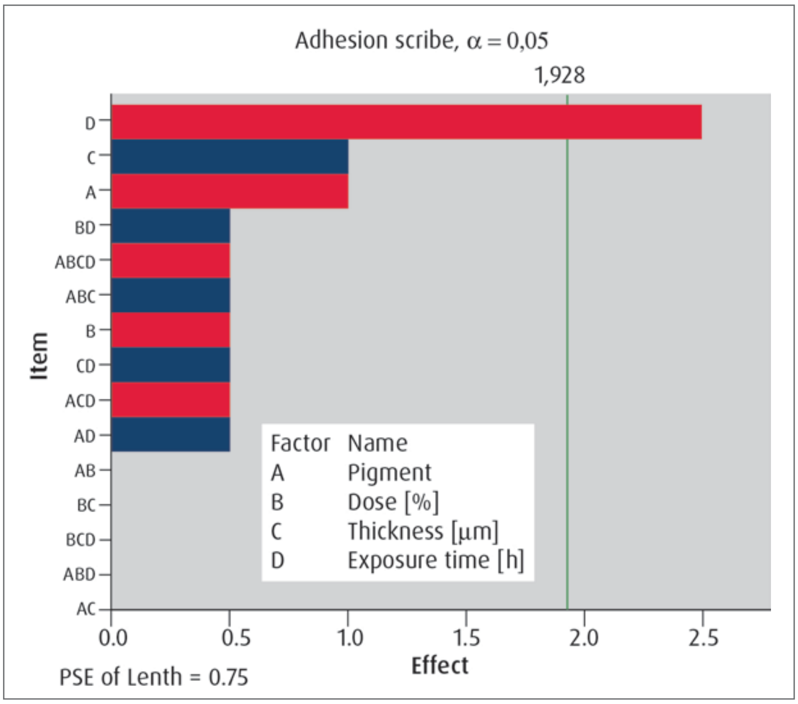

Figure 3: Pareto plot of effects (adhesion at the scribe, α = 0.05, PSE = Pseudo Standard Error)

Test procedures summarised

The performance of the zinc-free anticorrosive was compared with a standard zinc phosphate in a styrene-acrylic waterbased primer. The two pigments were tested at two different loading levels and at two different dry film coating thicknesses, to study their effectiveness in different conditions. Four paints (*Table 1*) were formulated containing each anticorrosive pigment at two different dosages: 3 % and 6 % of anticorrosive pigment in the dry film volume.
The paint formulas were calculated by keeping the same volume solids percentage (41 %) and the same PVC/CPVC ratio (0.47) in order to compare the pigment effect at the same free binder volume level. Due to the different oil absorption of these anticorrosive pigments, the amount of filler was changed to keep these parameters constant. This formulation method ensures that the differences observed are caused only by the pigment, not by differences in free binder volume level. It is well known that coating performance depends on the free binder volume level (measured by the PVC/CPVC ratio), and it is always recommended to bear in mind the different oil absorption of the pigments in order to keep a suitable free binder volume in each formulation.
The formulation was divided into a millbase for pigment dispersion, and a letdown with resin and additives to complete the paint and adjust viscosity and pH. The millbase was designed for a grinding process with glass balls of 3 mm diameter as a grinding element, and it was processed in an orbital shaker for 20 minutes to ensure a good fineness of grind.

Salt spray test procedure

A single layer of paint was applied on four standardised cold rolled steel panels ("S-46" grade from Q-Panel) at

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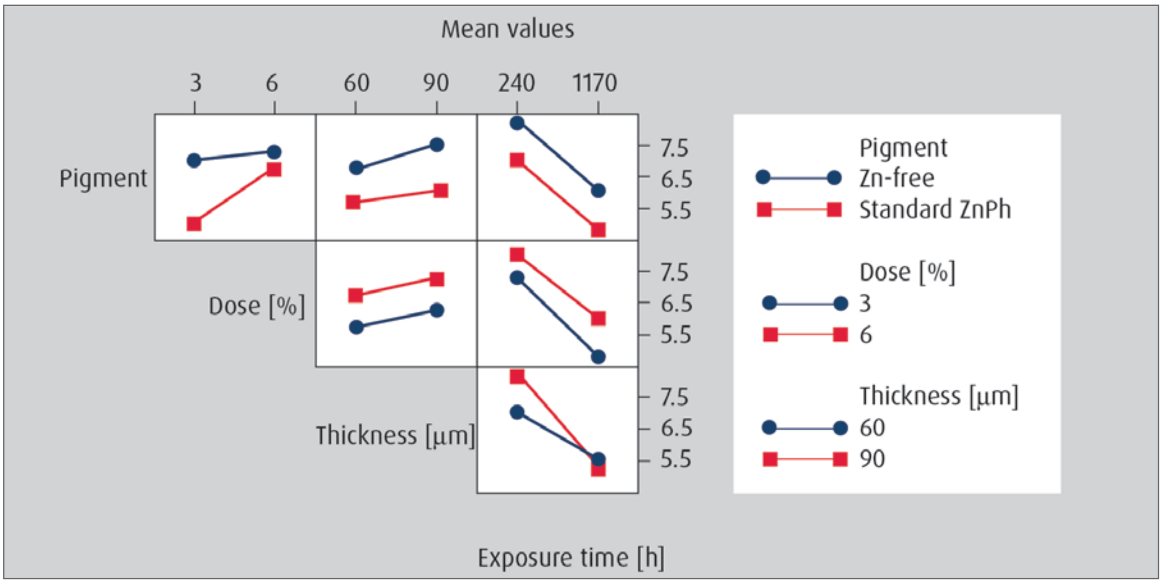

Figure 4: Interaction plot for oxidation at the scribe

two different dry film thickness, 60 µm and 90 µm, using application bars of 150 µm and 250 µm respectively. Thus two sets of eight panels with anticorrosive pigment at two different dosages and at two different dry film thicknesses were obtained.

Panels were dried for three weeks at room temperature before the salt spray test. Just before starting the test, panels were scribed with a single vertical cut of 6.5 cm, penetrating all the organic coating and leaving the metal uncovered in the cut. The salt spray test was performed according to ASTM B-117 [3], introducing the scribed samples into a salt fog spray chamber where a fog was created with a 5 % (by weight) solution of NaCl in water.

One set of panels was exposed for 240 hours, when the first significant differences between panels were observed. The other set was exposed for 1170 hours, when coatings with the best performance started to fail. After salt spray exposure, samples remained 24 hours at room temperature before coating performance evaluation.

At the scribe, the corrosion process has been forced (forced anode) and it allows an evaluation to be made of how the coating protects the metal once the corrosion process is on-going. So, by measuring the width of corrosion at the scribe, the effectiveness of the anticorrosive pigment in slowing down corrosion can be seen. Also, the loss of adhesion at the scribe can be related to the cathodic delamination.

The corrosion observed on the rest of the panel is due to electrolyte penetration through the coating, and is related to coating permeability. Once the water reaches the surface, the corrosion process starts, and again the effectiveness of the anticorrosive pigment in slowing down corrosion can be seen by measuring the total rusted area.

So the anticorrosive properties of each coating were evaluated by measuring the loss of adhesion and the rusted area both at the scribe and in the rest of the panel. Measurements were carried out according to the following ASTM standards:

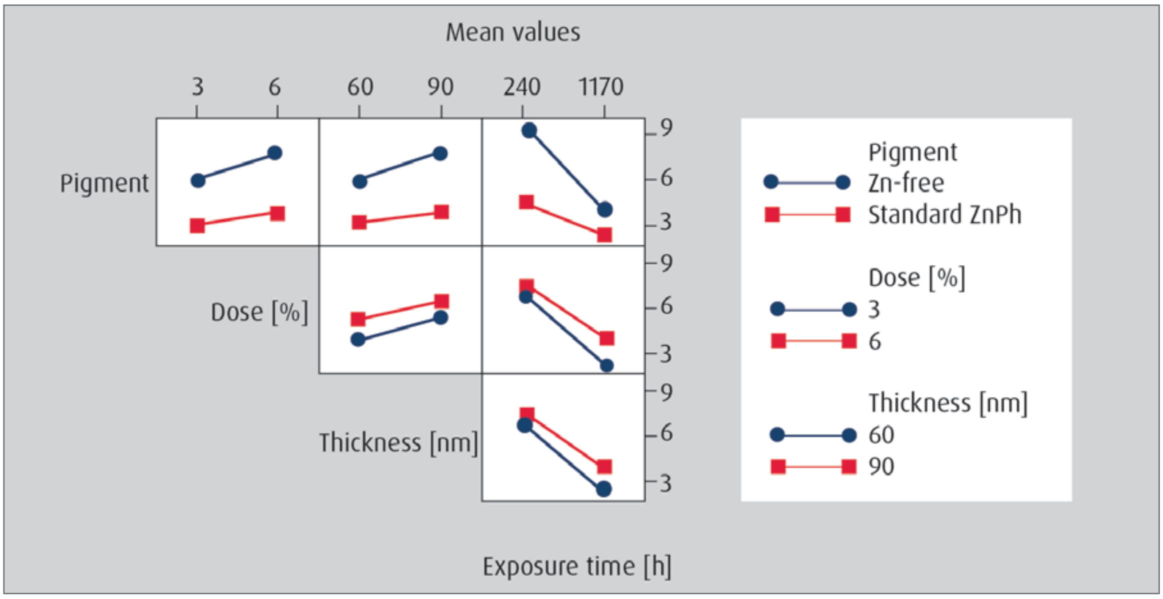

Figure 5: Interaction plot for oxidation on the panel

- Oxidation on the panel was measured according to ASTM D610-01.
- Oxidation and adhesion at the scribe were measured according to ASTM D1654-91, (A) and (B) respectively.

Statistical evaluation of results

For the present study a 2^4 factor experiment design was chosen. In this type of DOE each factor has two levels, and the factors can be quantitative, qualitative or both. Four factors were defined, three of them quantitative (film thickness, pigment concentration and exposure time) and one qualitative factor involving the nature of the pigment. The experiment involved 16 runs of one replication in one block. "Minitab 16.1.0" was chosen as a tool for DOE data processing. The results obtained for the oxidation on the panel (ASTM D610-01) and for oxidation and adhesion at the scribe ASTM D1654-91 are presented in *Table 2*.

The data processing with the programme gave Normal Probabilistic results (for significance level $\alpha = 0.05$) for the principal factors. These results can be seen in the form of Pareto plots showing the relative importance of the main factors and interactions (*Figures 1-3*) and in the more visual interaction plots of *Figures 4* and *5*.

As expected the main principal factor was the exposure time; nevertheless, the rusting is affected by the nature of the kind of pigment (A), being primary in the case of the oxidation on the panel and more significant than the thickness (C) or the amount (B) in the case of the oxidation at the scribe.

Finally, the adhesion at the scribe was not affected by the kind of pigment (A). It depends on the time of exposure to salt spray, and due to this fact it can be related to cathodic delamination phenomena.

An interaction plot for oxidation at the scribe (*Figure 4*) shows how the zinc-free pigment prevented this oxidation at the scribe better at lower doses than the standard zinc phosphate; the thickness (90 µm) was relevant at low exposure time, becoming insignificant at high exposure time.

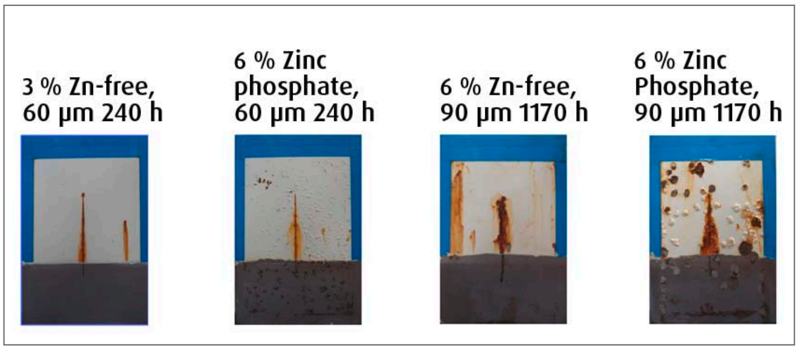

Figure 6: Salt spray test results showing the faster activity and higher efficiency of Zn-free at 240 and 1170 hours of exposure in salt spray test

An interaction plot for oxidation on the panel (Figure 5) shows how the zinc-free pigment is more effective than standard zinc phosphate even at a lower dose and thickness. Initially (240 h) both pigments are different and over time (up to 1170 h) they become more similar; this fact can be related to the higher solubility of the zinc-free pigment (15 mg/100 ml) compared to the standard zinc phosphate (3 mg/100 ml); this should lead to the first one acting faster. This emphasises the importance of the selection of the anticorrosive pigment and how this effect can be promoted if the dose is increased. *Figure 6* shows some panels confirming this fact.

REFERENCES

[1] *Vetere V. F. et al*, Calcium tripolyphosphate: an anticorrosive pigment for paint, JCT, 2001, Vol. 73, pp 57-63 (and references within).

[2] *Antony J.*, Design of Experiments for Engineers and Scientists, Butterworth-Heinemann Oxford, Burlington, MA, USA, 2003.

[3] ASTM B117 – 11, Standard Practice for Operating Salt Spray (Fog) Apparatus.

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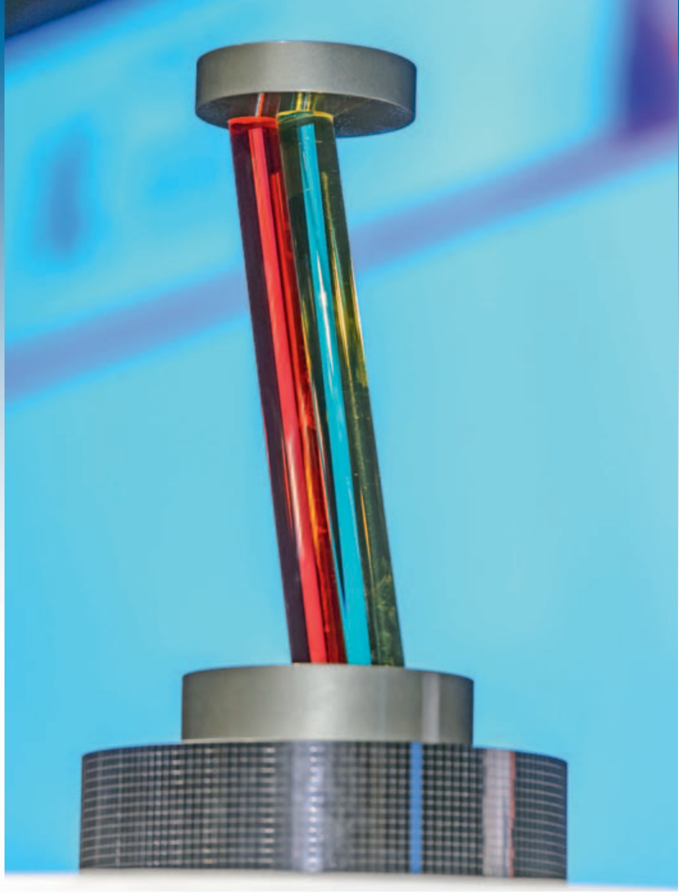

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