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Pigments & Additives
Research & Process developmen
7.2.07

New developments and concepts for high performance organic pigments

Clariant

Exactly your chemistry

Presentation in the event of COC 2007, Mumbai, 7.-9.2.07

Content

1. General introduction

2. Warpage in polyolefin colorations

3. Easily dispersible pigments for coating applications

4. Ultra-fine pigments

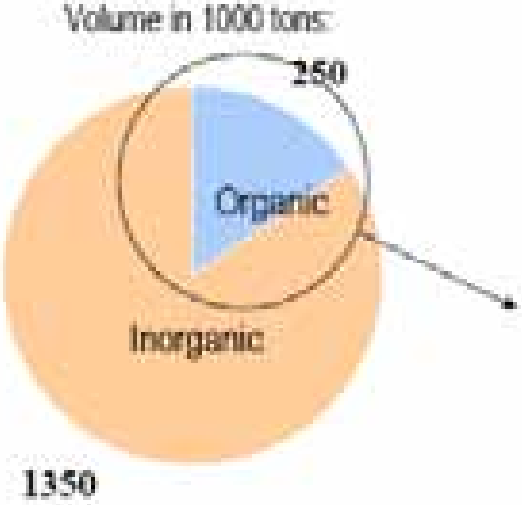
5. Conclusion

1. General introduction

History – Synthetic organic pigments

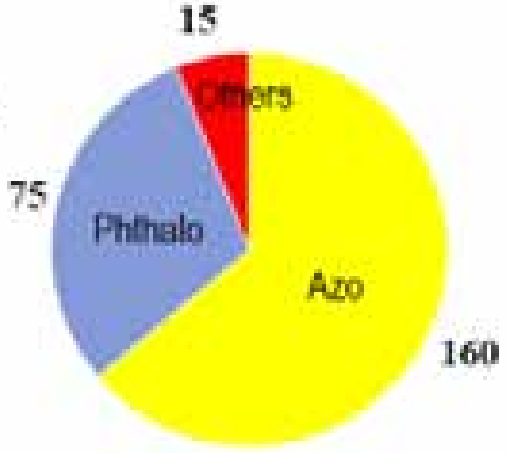
1885	beta-Naphtol Pigments
1909	Monoazo Pigments (HOECHST)
1912	Naphtol AS Pigments
1935	Diarylide Yellow Pigments
1935	**Phthalocyanine Blue (ICI)**
1939	**Phthalocyanine Green**
1952	Dioxazine Violet (HOECHST)
1954	Disazocondensation Pigments (CIBA)
1955	Quinacridone (DU PONT)
1960	Benzimidazolone Pigments (HOECHST)
1964	Isoindolinone Pigments (GEIGY)
1972	Isoindolinone (BASF; CIBA-GEIGY)
1986	Diketo Pyrrolo Pyrrole Pigments (CIBA-GEIGY)

Global market for pigments



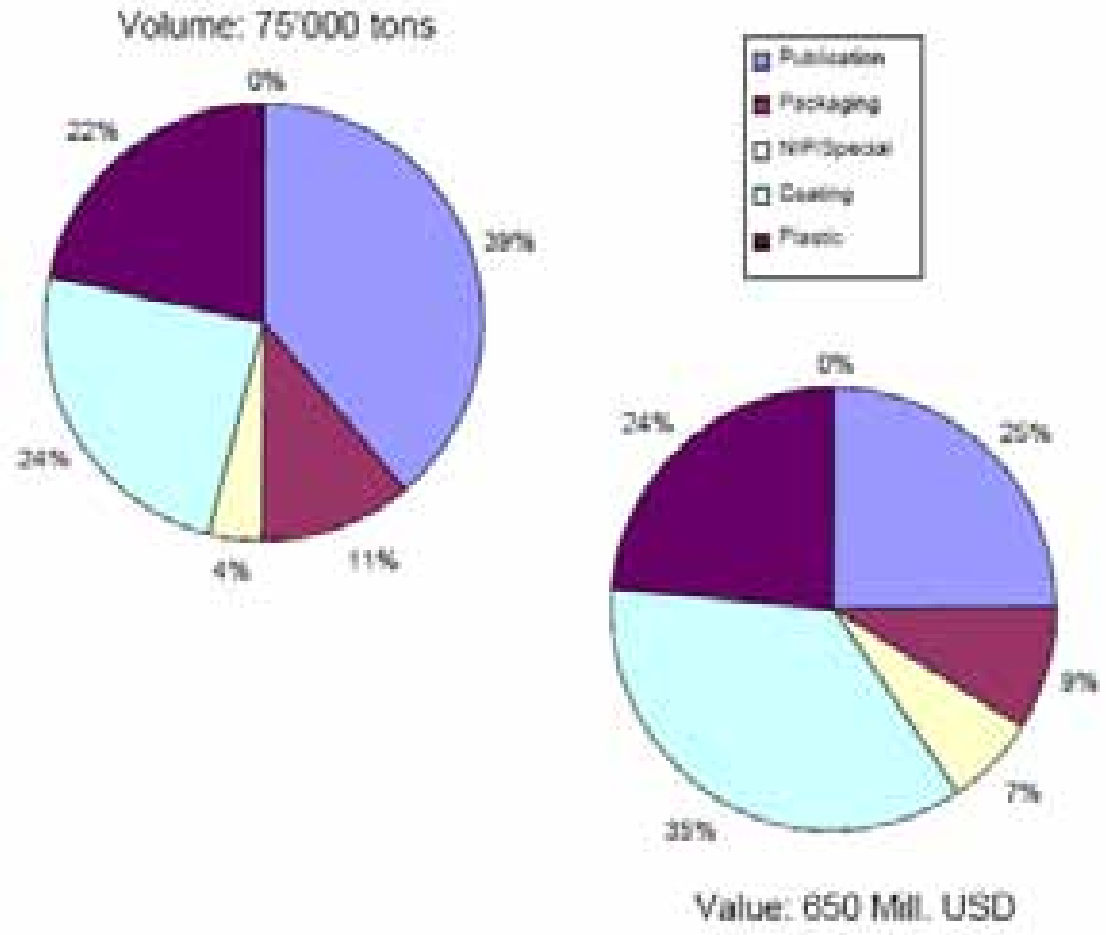
Global consumption of chromatic pigments in 2005: 1'600'000 tons

Market for chromatic pigments in Value:
Organic: 3'500 million USD
Inorganic: 1'900 million USD



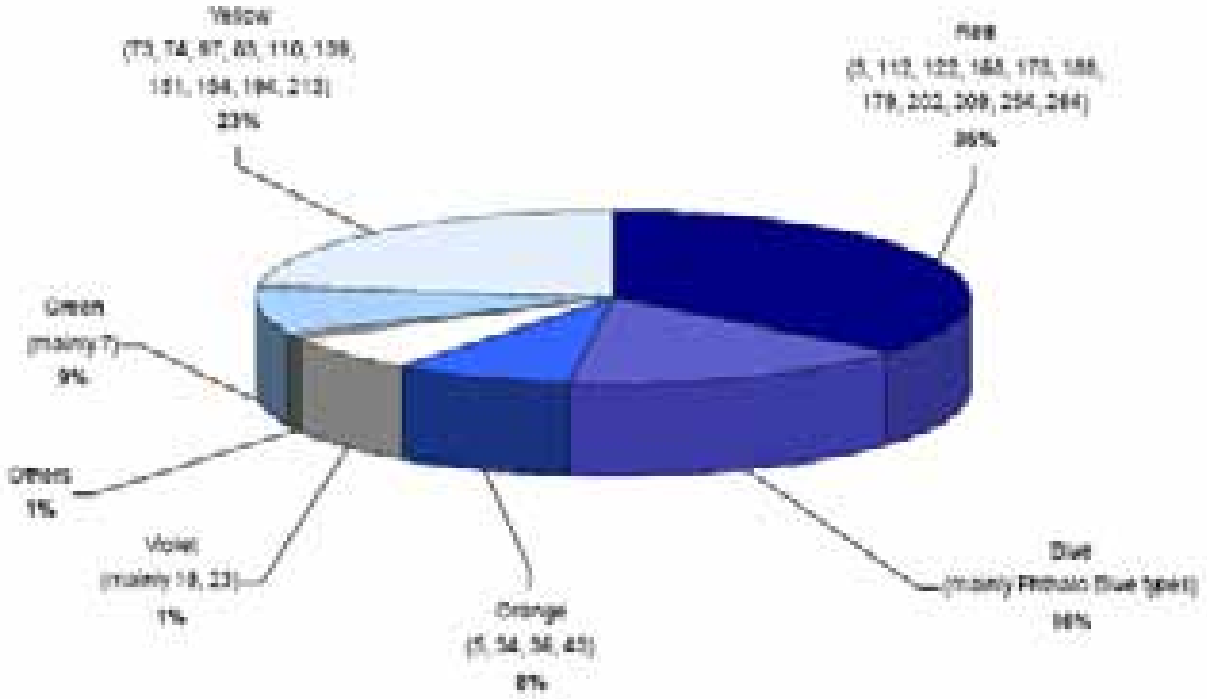
Azo: 160'000 tons with 237 C.I. items
Phthalo: 75'000 tons with 11 C.I. items
Others: 15'000 tons with 118 C.I. items
(Quinacridones, Perylenes, DPP, Thioindigos, Dioxazines, Anthraquinones, Quinophthalones)

*Global market for **Phthalo** pigments*



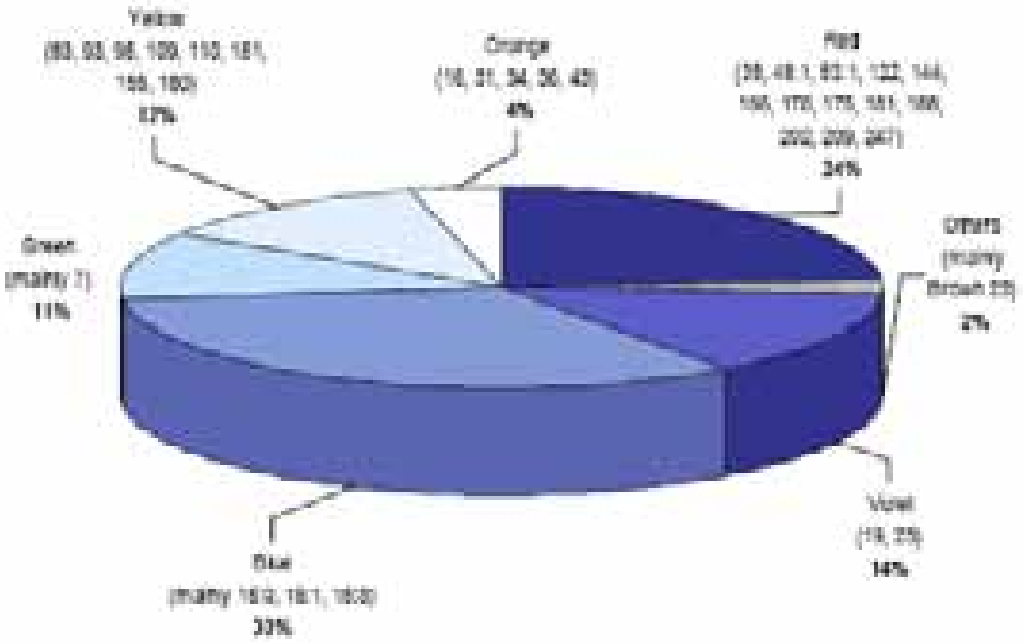
Consumption

Use of Organic Pigments in Coatings by Volume



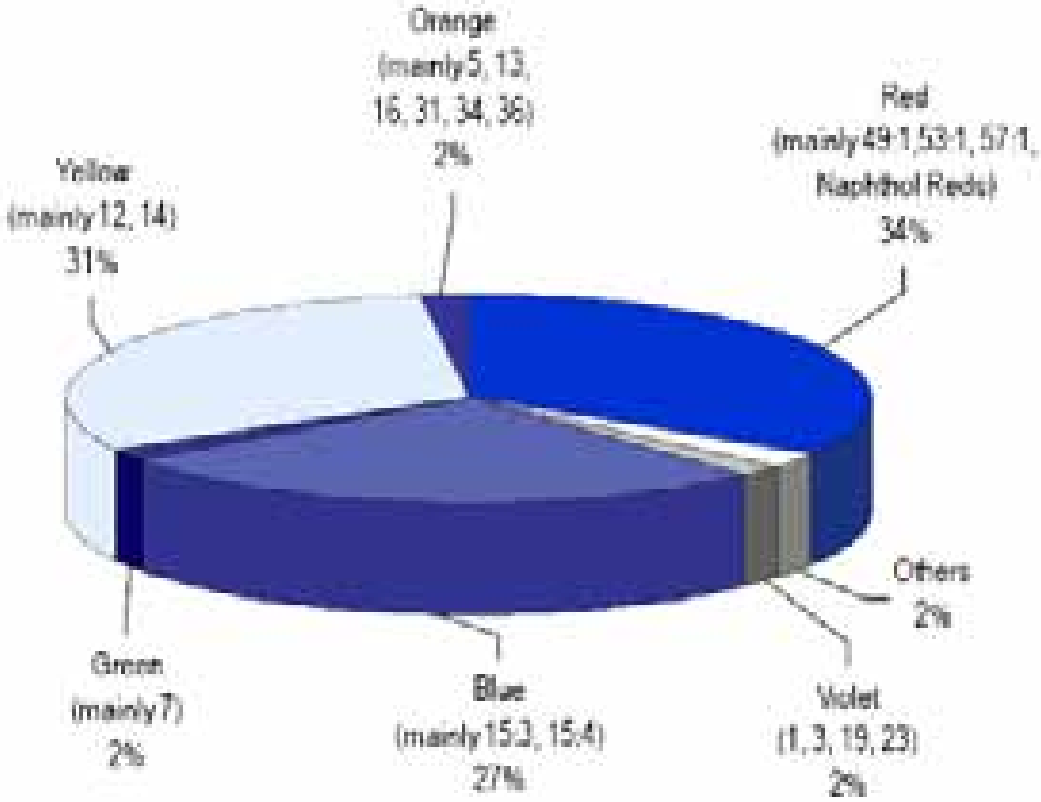
Consumption

Use of Organic Pigments in Plastic and Rubber by Volume



Consumption

Use of Organic Pigments in Printing Inks and Textiles by Volume



2. Warpage in polyolefin colorations

Injection molding

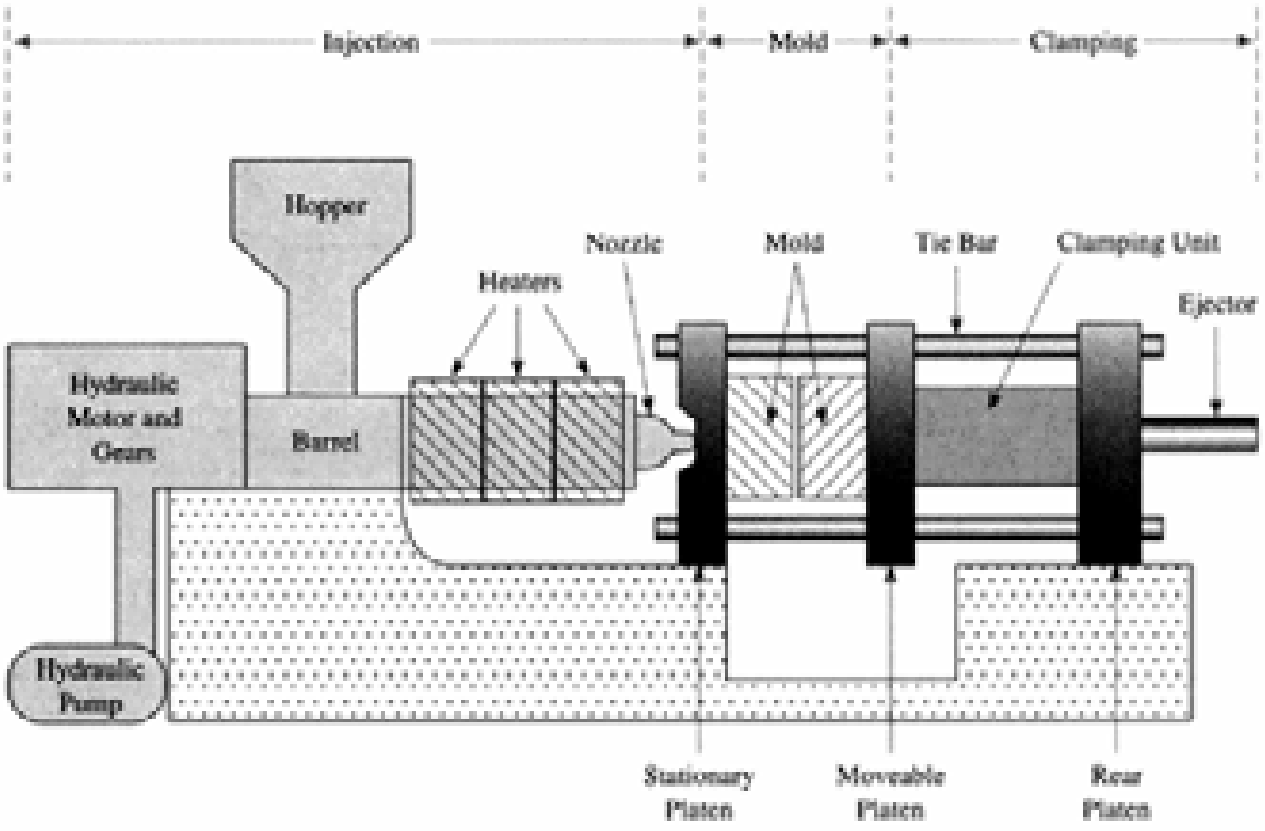
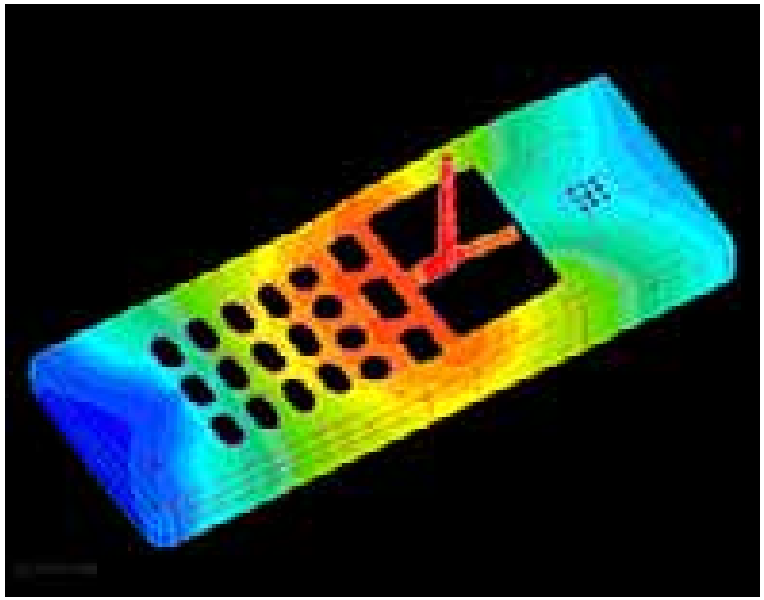


Figure 1 Injection molding machine showing three major functional units (injection, mold, and clamping) along with major components of each unit.



Anisothropic cooling

Bottle crates as example for high volume products

Options to avoid warpage effects

- engineering of cooling process : ensuring of homogeneous cooling

- extended stay of the product in the mold

- use of warpage-free pigments

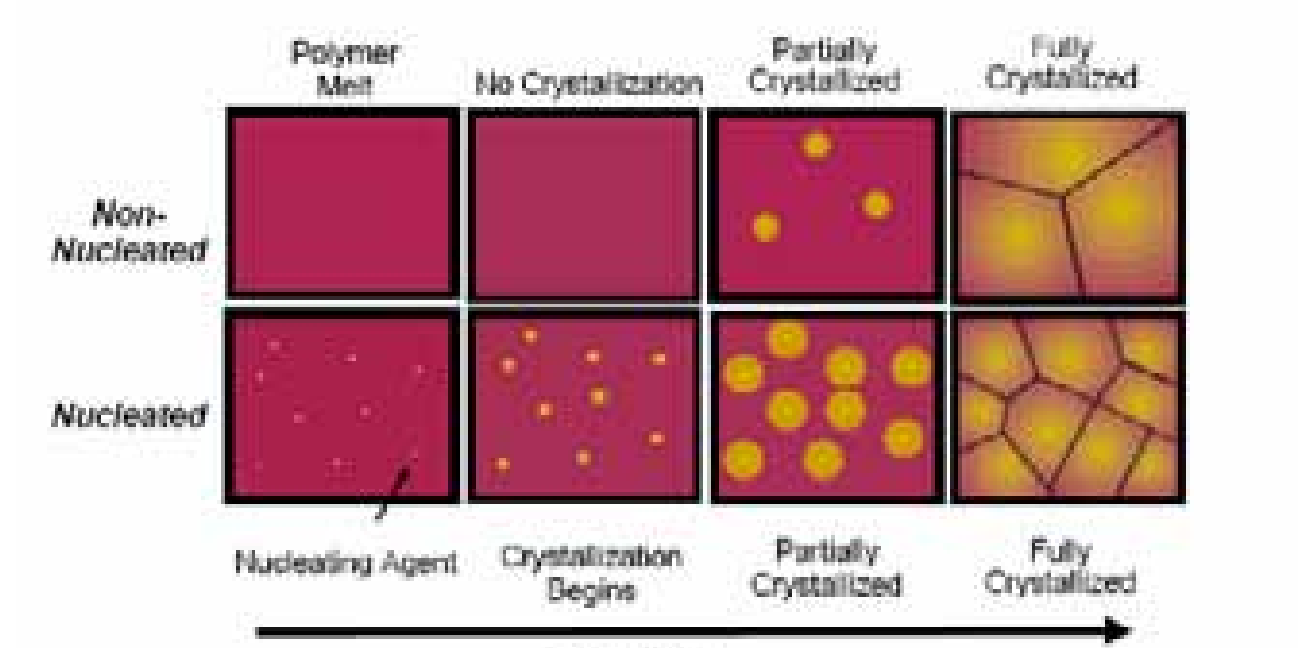
Theory of warpage – literature

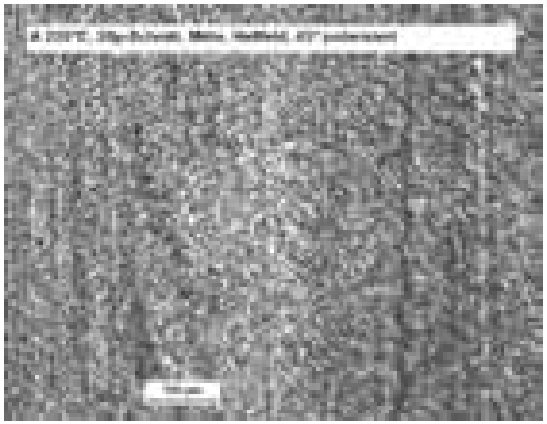
Differences of pure HDPE vs HDPE coloured with copper phthalocyanine

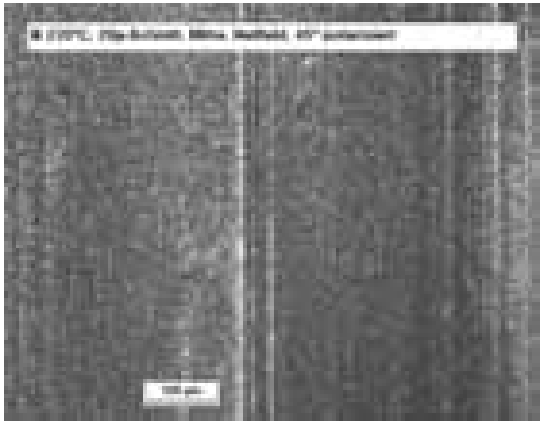
- Absolute crystallinity falls by 5% from 69%
- Amount of crystals is increased
- Size of the crystals is decreased
- Speed of crystallization of HDPE in presence of CPC is increased
- Crystallization temperature in the presence of CPC is increased
- In the presence of CPC the formation of fiber-like structures during injection-moulding is observed

P. E. Tomlins, M. J. Richardson, M. J. Shenton and J. J. Janimak, *The influence of pigments on the crystallisation behaviour, morphology and dimensional stability of plates injection moulded from high density polyethylene*, National Physical Laboratory Report CMMT(A) 217, April 2000.

Theory of warpage

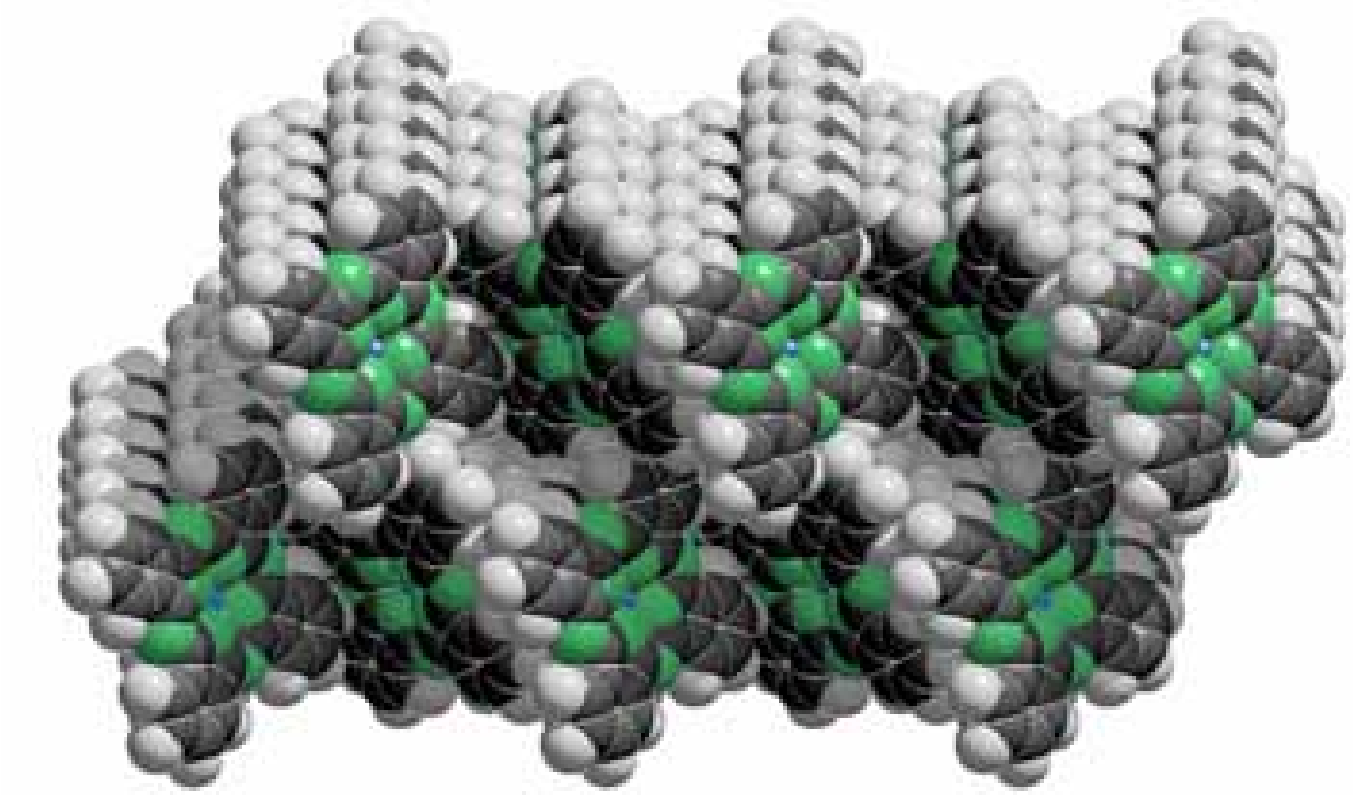






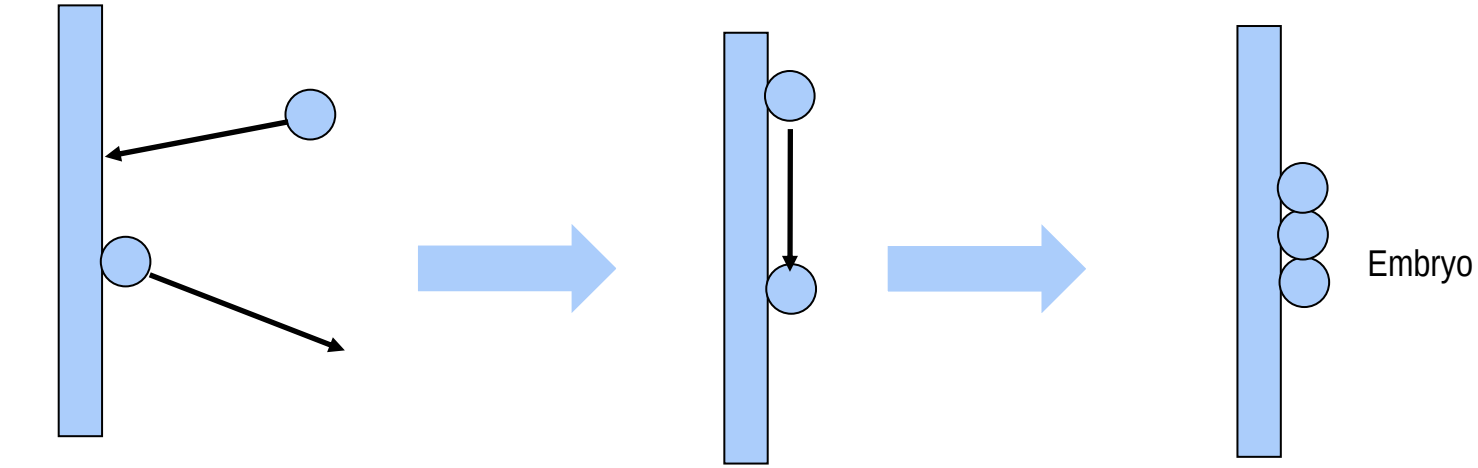
F. L. Binsbergen Progr. Solid State Chem. Bd. 8,189-238

Structure of a copper phthalocyanine



On the surface of pigment crystals the nonpolar groups form parallel ditches enabling accomodation of polyethylene chains, thus reducing the free energy of the formation of the critical nucleus.

J. Broda, J. Appl. Polymer Sc., *90*, 2003, 3957-3964.

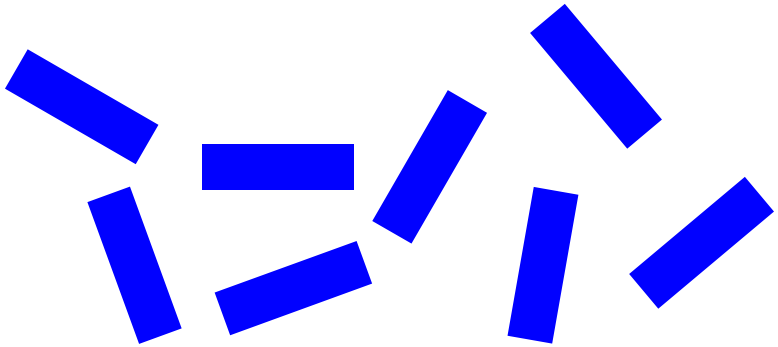


Adsorption and Desorption

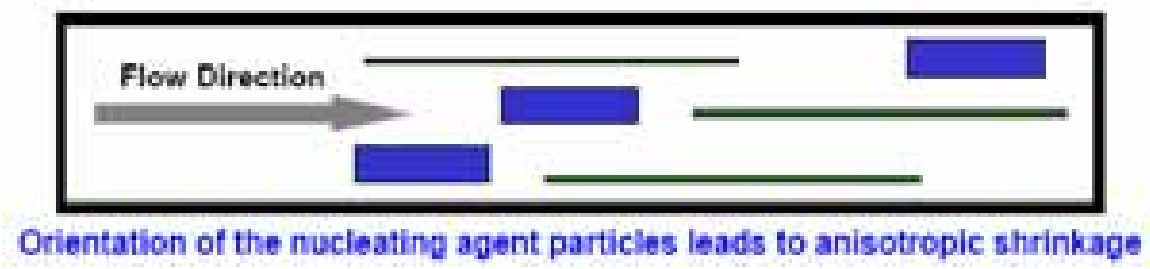
Migration

In the shallow ditches of the CPC crystal
Polymer nuclei are preformed

Theory of warpage



In the molten polymer the pigment is disordered



Orientation of the nucleating agent particles leads to anisotropic shrinkage

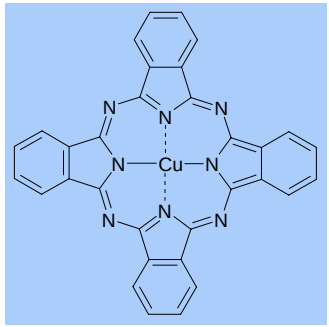
Own investigations

- Visualisation of warpage by optical methods

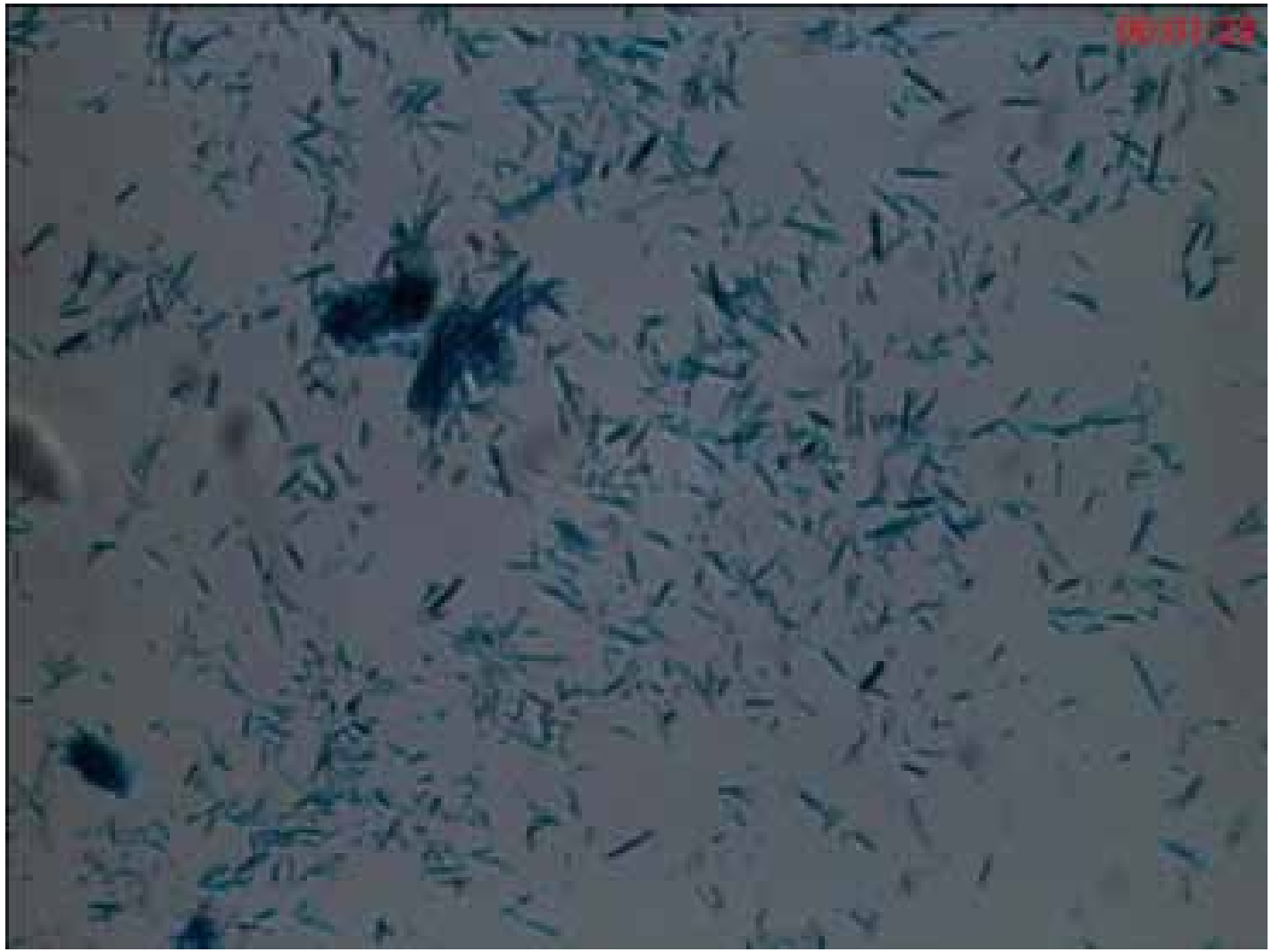
- Preparation of CPC crystals of the size of 10 microns

- Studies of crystallization at 126° C / HDPE at
  „ Deutsches Kunststoffinstitut Darmstadt“

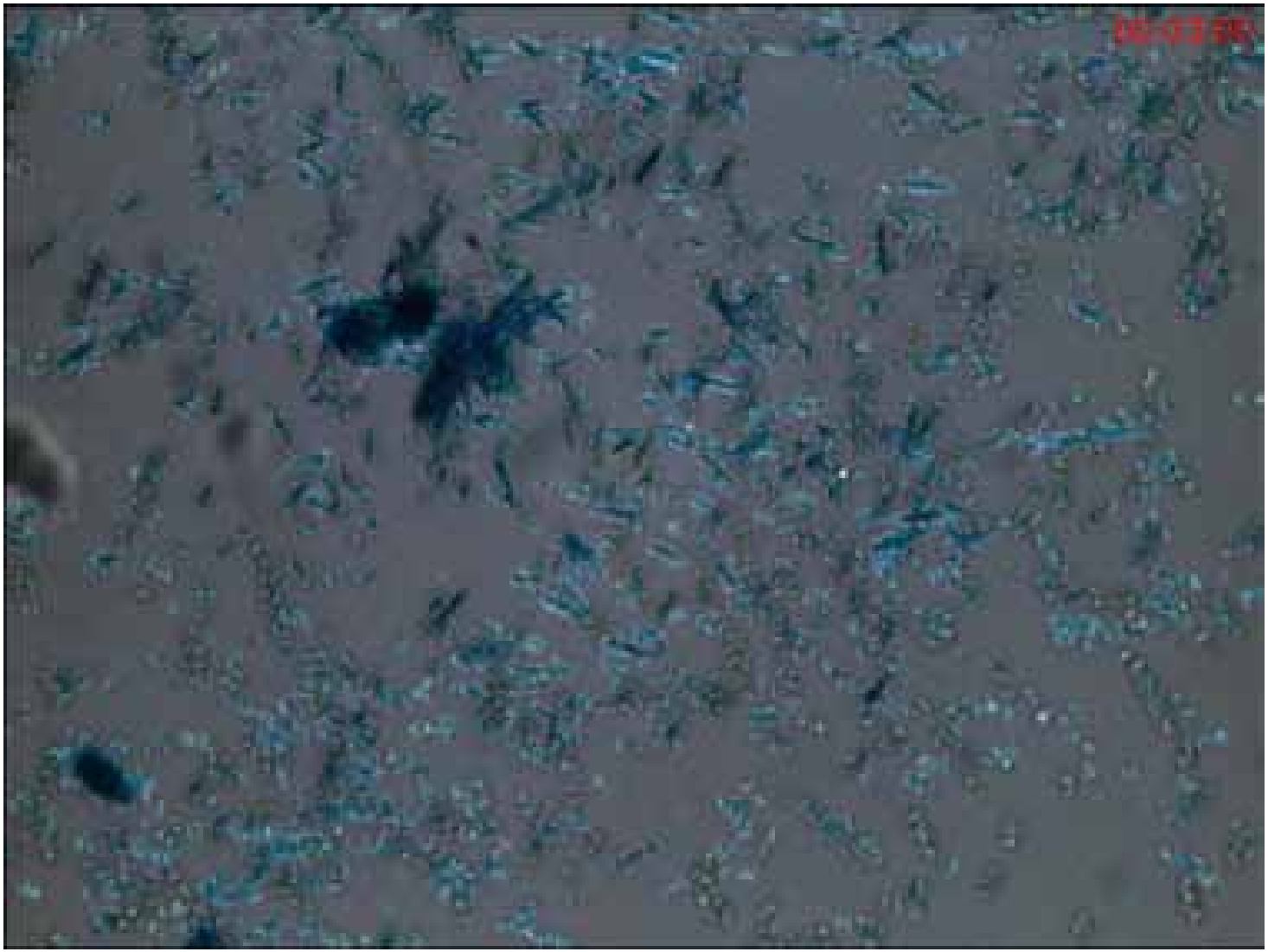
CPC =



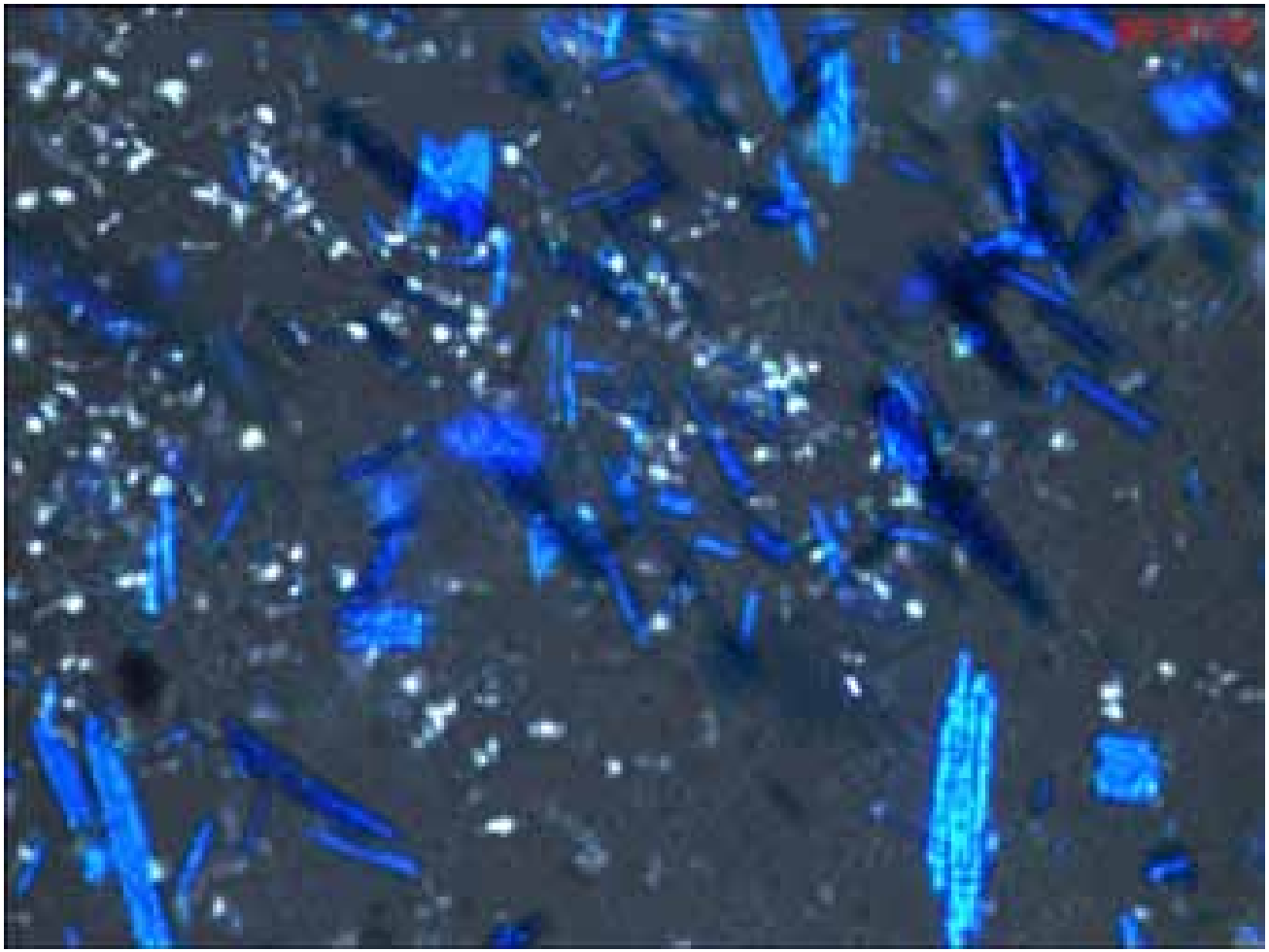
Structure of copper phthalocyanine



Structure of copper phthalocyanine



Structure of copper phthalocyanine



Summary

- Warpage is caused by nucleating of pigment crystals

- Unpolar crystal faces of pigments form nuclea

Possible counteractions

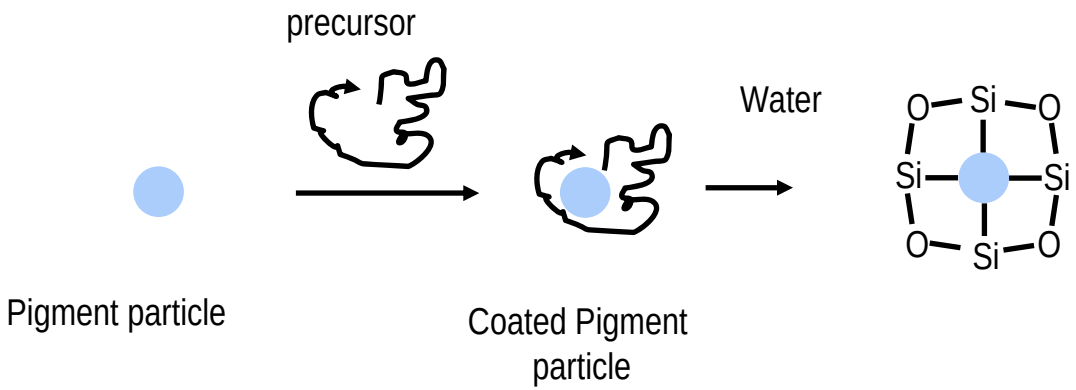
- Encapsulation of pigments

- Additives that tightly stick to pigment surfaces and do not allow nucleation

- Development of new warpage-free pigments

Encapsulation of organic pigments with silica

Principle:



limited success on reducing warpage

reason: friction during shearing may destroy silica shell

Concept of encapsulatin pigments with organic polymers

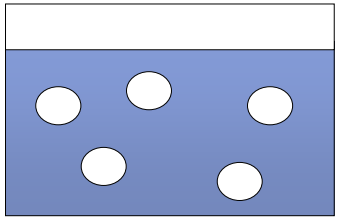
Monomer(s) / hydrophobe / (initiator)

Surfactant in water

stirring

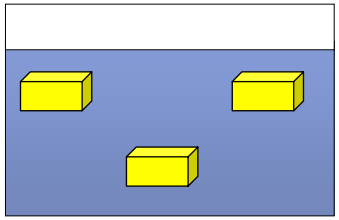
Pre-emulsion

high shear

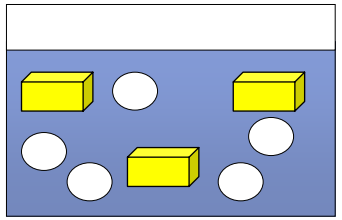


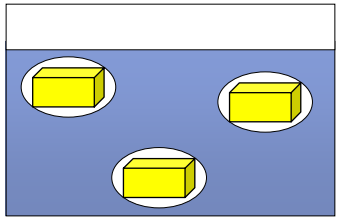
Monomer-miniemulsion

Pigment-dispersion



1. stirring,
2. high shear → fusion / fission

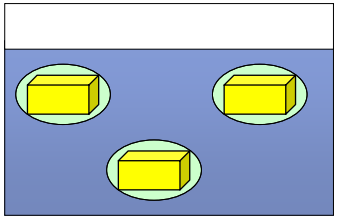




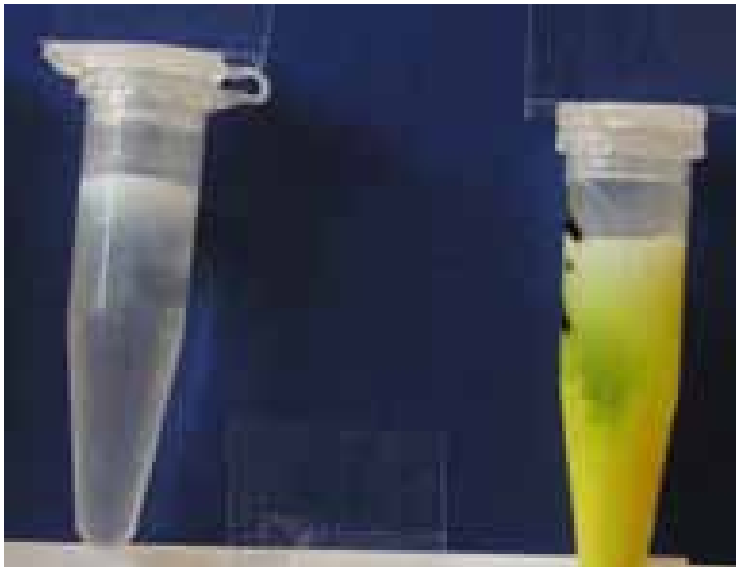
Pigment with monomer coating, dispersed in water

heating (+ initiator) (polymerization)

Dispersion of polymer-encapsulated pigment



Encapsulation of pigments



polystyrene

pigment / polystyrene

Benefits

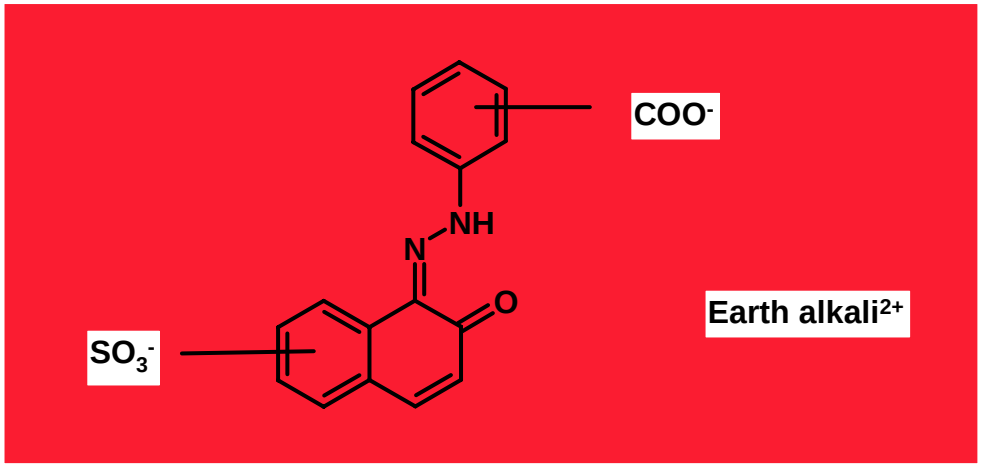
- alteration of surface
- many variations possible
- tool for tailor-made solutions

Drawbacks

- isolation of particles difficult
- high costs compared to powder pigments

New warpage-free pigments

Example : C.I. Pigment Red 285



Medium-red hue
High temperature stability
Warpage-free

Conclusion

- Warpage is an important field for innovation
- Reason is well understood
- New pigments are released into the market
- Additives allow to modify existing pigments

2. Easily dispersible pigments for coating applications

Pigment dispersions

Liquid pigment dispersions

- perfect dispersibility and and compatibility with paint systems
- high transport costs of solvent/water
- cleaning costs

Solid pigments dispersions

- good dispersibility in most paint systems (water or solvent)
- high manufacturing costs
- requirement for new equipment when replacing liquid systems

Concept of easily dispersible pigments

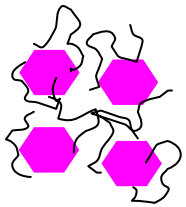
Pigment

(≥ 80%)

Dispersing Agent

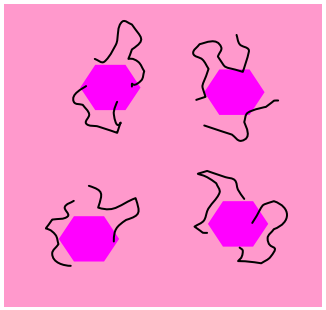
1.Surface Treatment

2.Isolation

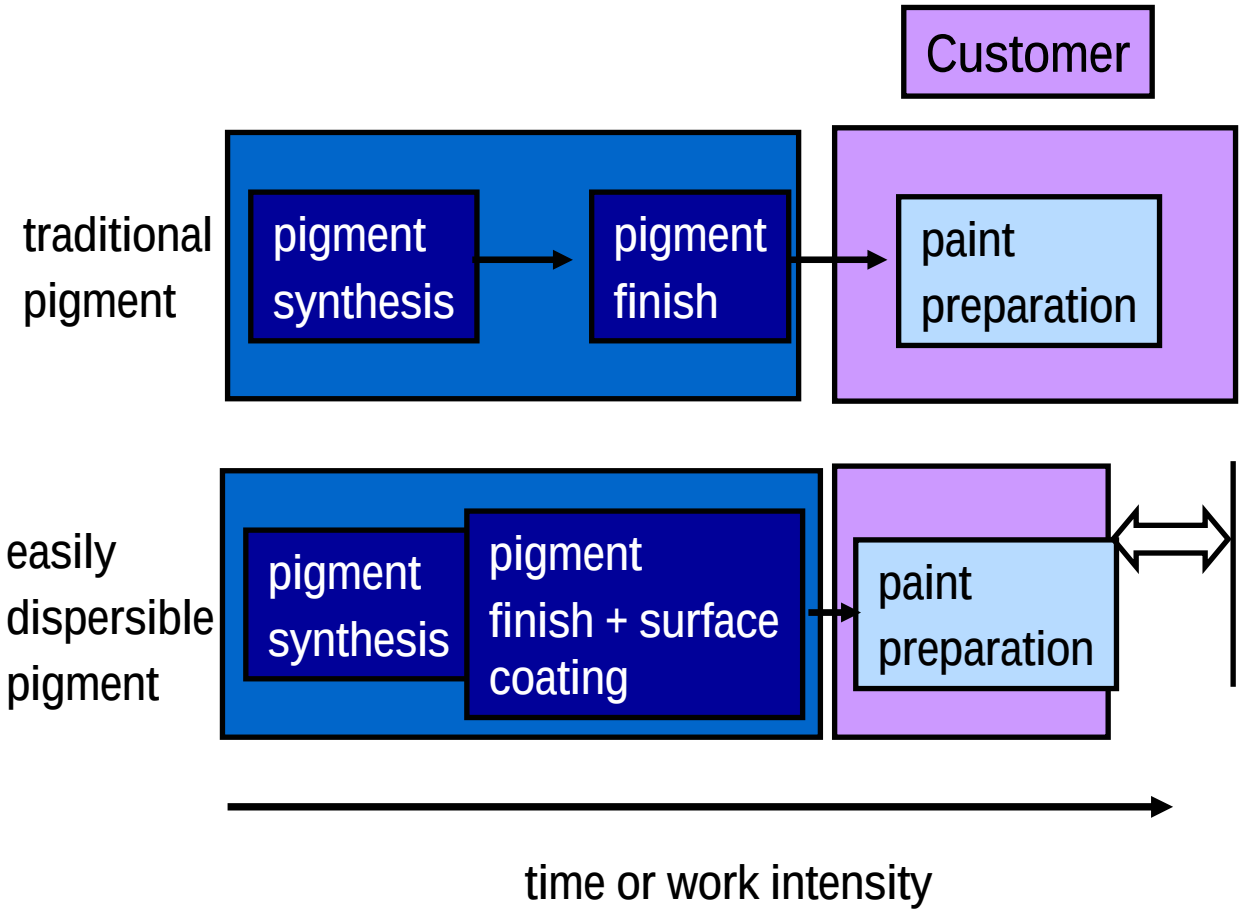


Stir-in Pigment

Easily Dispersible



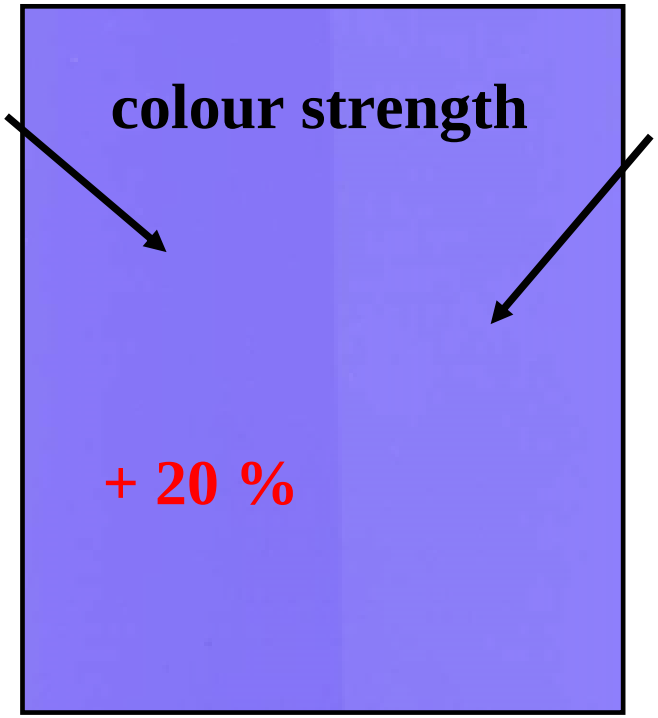
Concept of Stir-in Pigments



Gain of colour strength of easily dispersible pigments

coated pigment

paint prepared
by use of a
dissolver



**P.V. 23 –
commercial grade**

Paint prepared
by use of a
Pearl mill

Stoving enamel alkyd melamin paint

Conclusion

- The use of polymers in the pigment process enhences dispersibility

- Easily dispersible pigments avoid additional preparation steps

- Easily dispersible pigments are limited for solvent paints up to now

- A good compatability with most paint systems is achived

- Pearl milling is not any more requirde on use of these new powder pigments

4. Ultrafine Pigments

Requirement for ultrafine pigments for

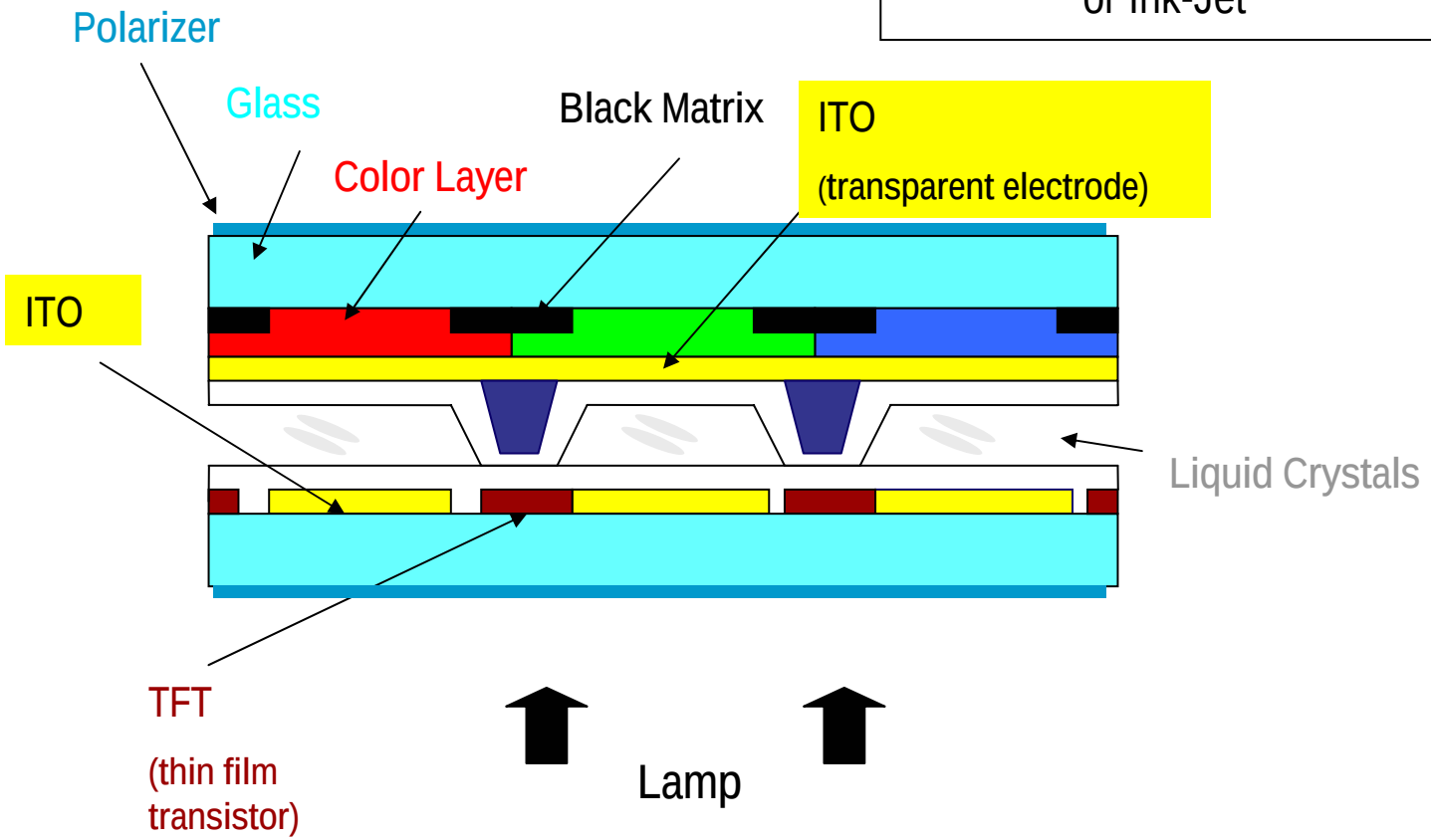
- Ink application if high transparency is required

- Color filter applications

- ???

TFT LCD (Thin Film Transistor Liquid Crystal Display) Schematic

Manufacturing Method:
For example: Photolithography or Ink-Jet



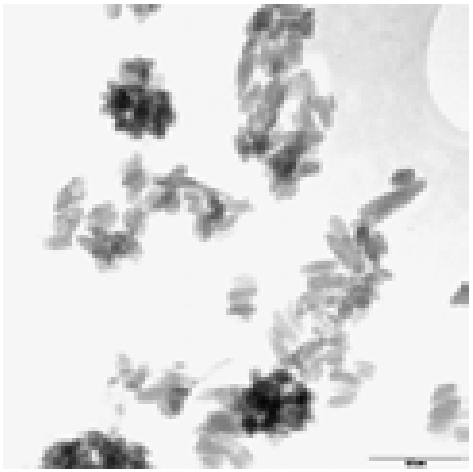
Pigments applied in Colorfilters

	Main component	Shading components for TV	Shading components for Cell Phones
		[Note PC]	
Red	P.R. 254	P.R. 177	P.Y. 139
Green	P.G. 36	P.Y. 150	P.Y. 138
Blue	P.B. 15:6	P.V. 23	
		High contrast Thin film strong color	High Y value Low power consumption high brightness

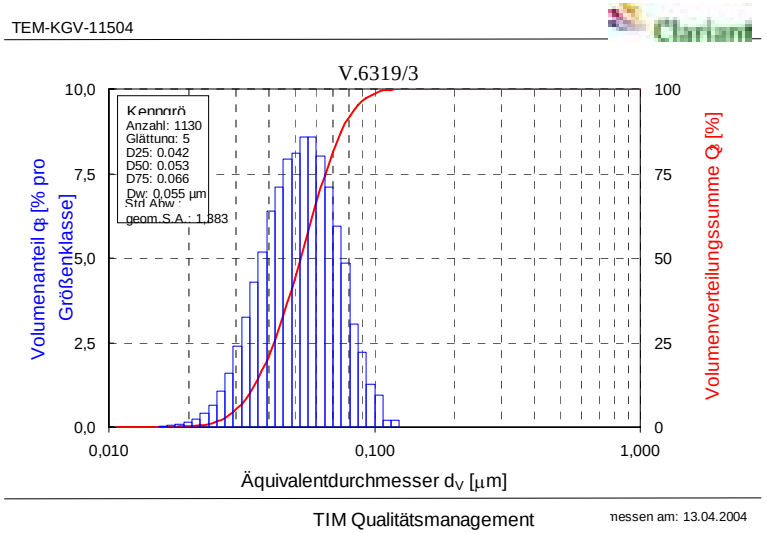
Pigments for Colorfilters - requirements

1. Particle size below 100 nm, narrow distribution

2. Excellent dispersibility



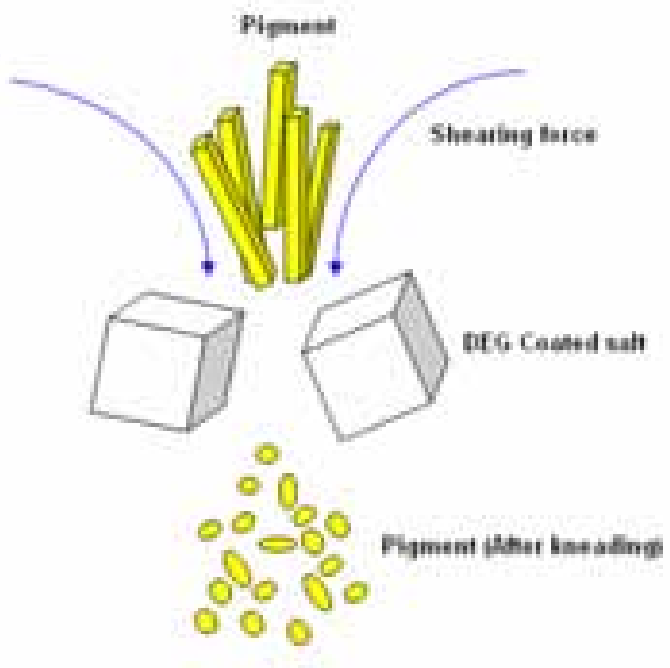
200 nm



Process of Saltkneading

Grinding of pigment with salt
In presence of a solvent:

- Extreme shear-forces
- Provides ultra-fine particles



Disadvantages:
- Waste
- High energy demand
- Low productivity

Industrial process for obtaining ε-CPC

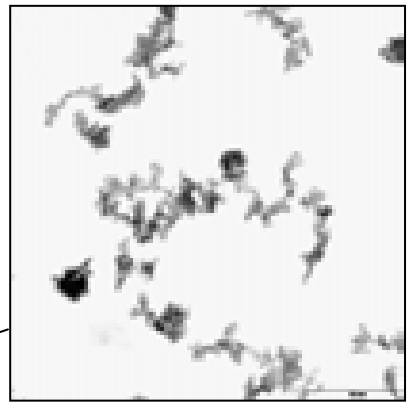
α-CuPc (milled)

Solvent-treatment

ε-CuPc

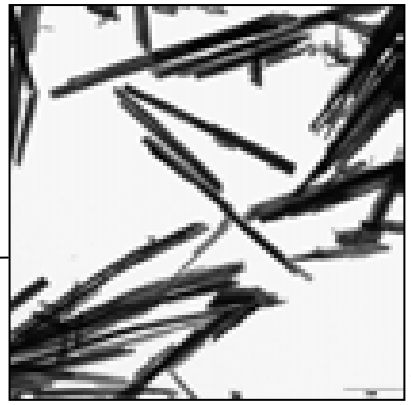
unwanted phase-change

β-CuPc



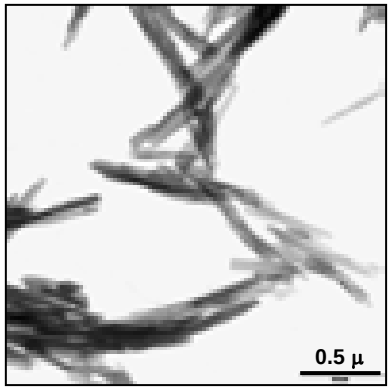
10000x

10000x



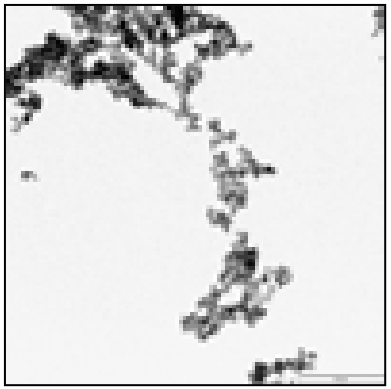
5600x

Goal: Obtaining microcrystalline ε-CuPc without milling



Phase-stabilizer only

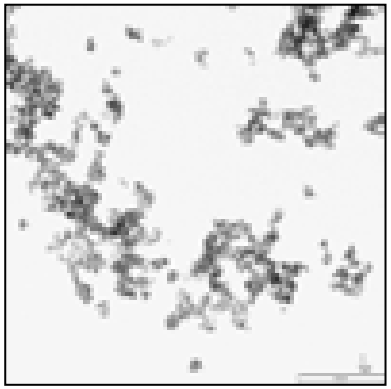
Saltkneading



Milled pigment
(α/ε-mix)

?

Phase-stabilizer
and
Growth inhibitor



Ultrafine grade

Challanges in the developent of ultra-fine particles

- Obtaining pigments in narrow particle size distribution

- Ensuring good dispersibility inspite of huge surfaces

- Avoiding milling / grinding operations if possible

- Ensuring large quantity production

5. Conclusion

Conclusion

High Performance Pigments have a lot of innovative potential

New application require new forms of pigmnets

Observation of cost is always important

Acknowledgement

Clariant for support

My coworkers for constant engagement

Organizing commitee of COC 1007 for invitation

Audience for kind attention