Sustainable, Mineral based Auxiliaries for the wet processing of textiles

Solutions for Oligomer Problems in Dyeing Polyester

Introduction

Past:

- Many years ago, raw sewage was dumped into rivers

Nowadays:

- Effluent treatment by mills and communities
- Much attention for harmful substances
- Renewable, biodegradable raw materials as bases for products and polymers
- Recycling of process water
- Use of minerals, such as clays?

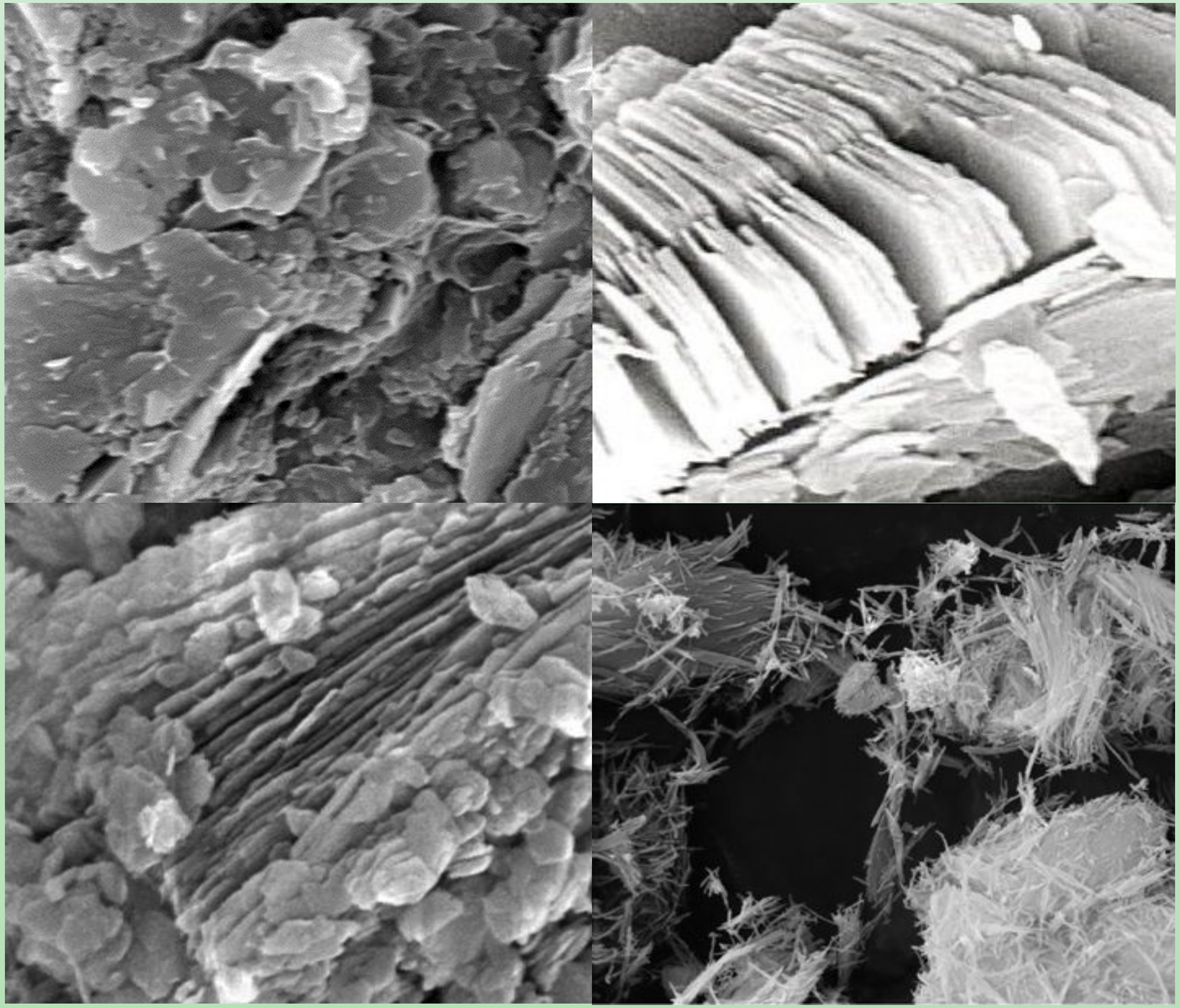
Applications of clays

- Industrial applications:
  - Construction
  - Drilling fluids
  - Foundry (molding sands)
  - Ponds, landfills
  - Reinforcement of plastics and fibres (organo-modified)
  - Catalysts
  - Stabilizers for paints (organo-modified)
- Cosmetic products
- Paper industry
- Refining (oil, wine)
- Textile industry used clays for cleaning and felting wool (Fuller's earth)
- Sedimentary clays are still widely used for washing (in rivers)

Manifold types of clay

- Basic elements: Si, O, Al, Mg, Ca, (Fe, Li, K)
- Many types of clays formed by weathering rocks (sedimentary clay) and weathering volcanic ashes (specific species)
- Type: > ratio of the different elements in deposits
- Clays have varying properties
- Interesting > Phyllosilicates (flexible sheet-like shape)
- Have more or less strong negatively charged surface

Clay-Structures



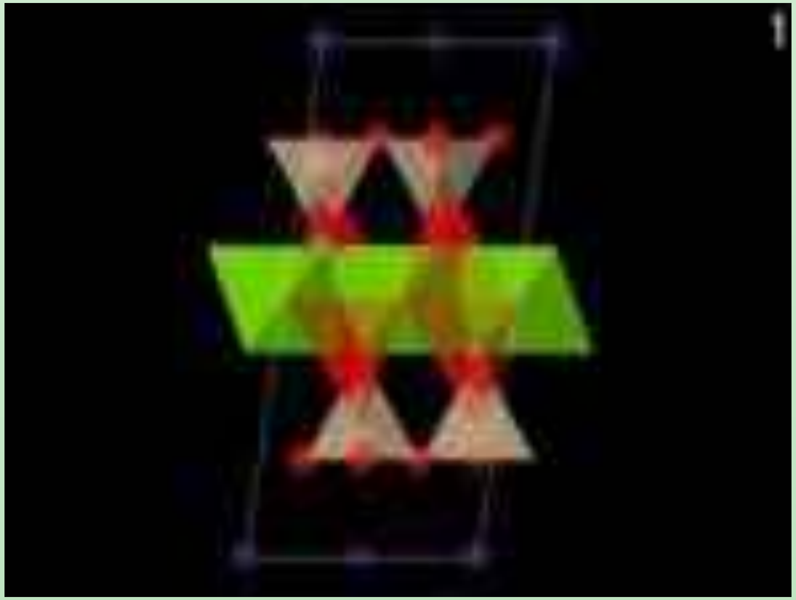
Crystal structures

Layered crystal tetrahedral and octahedral structures, e.g.:

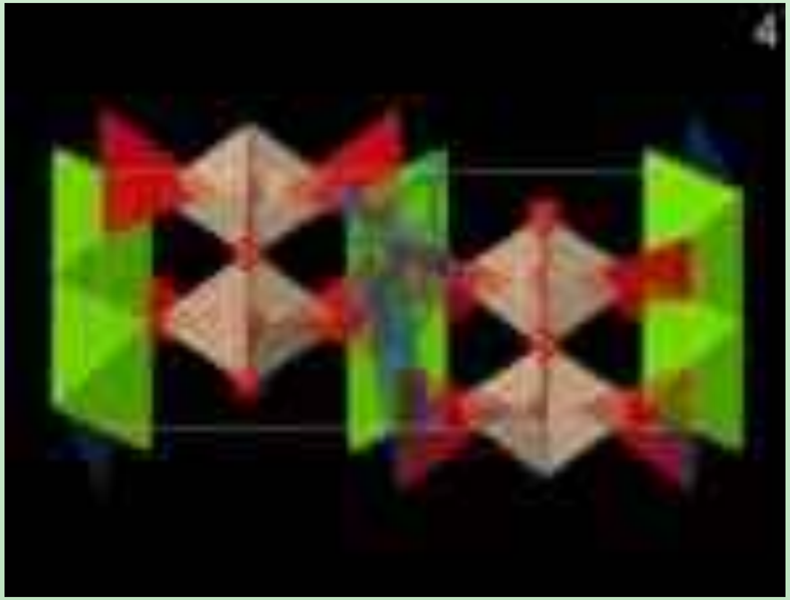
- **kaolinite**, 1 tetrahedron + 1 octahedron (sheet)
- **illite**, 2 tetrahedrons (sheet)
- **chlorite**, tri-octahedral (sheet)
- **smectite**, 2 terahedrons and central octahedron (sheet)
- **sepiolite**, rows of double tetrahedrons (needle)

- (Also mixed layers and mixed clays are found)

Some examples



Hectorite

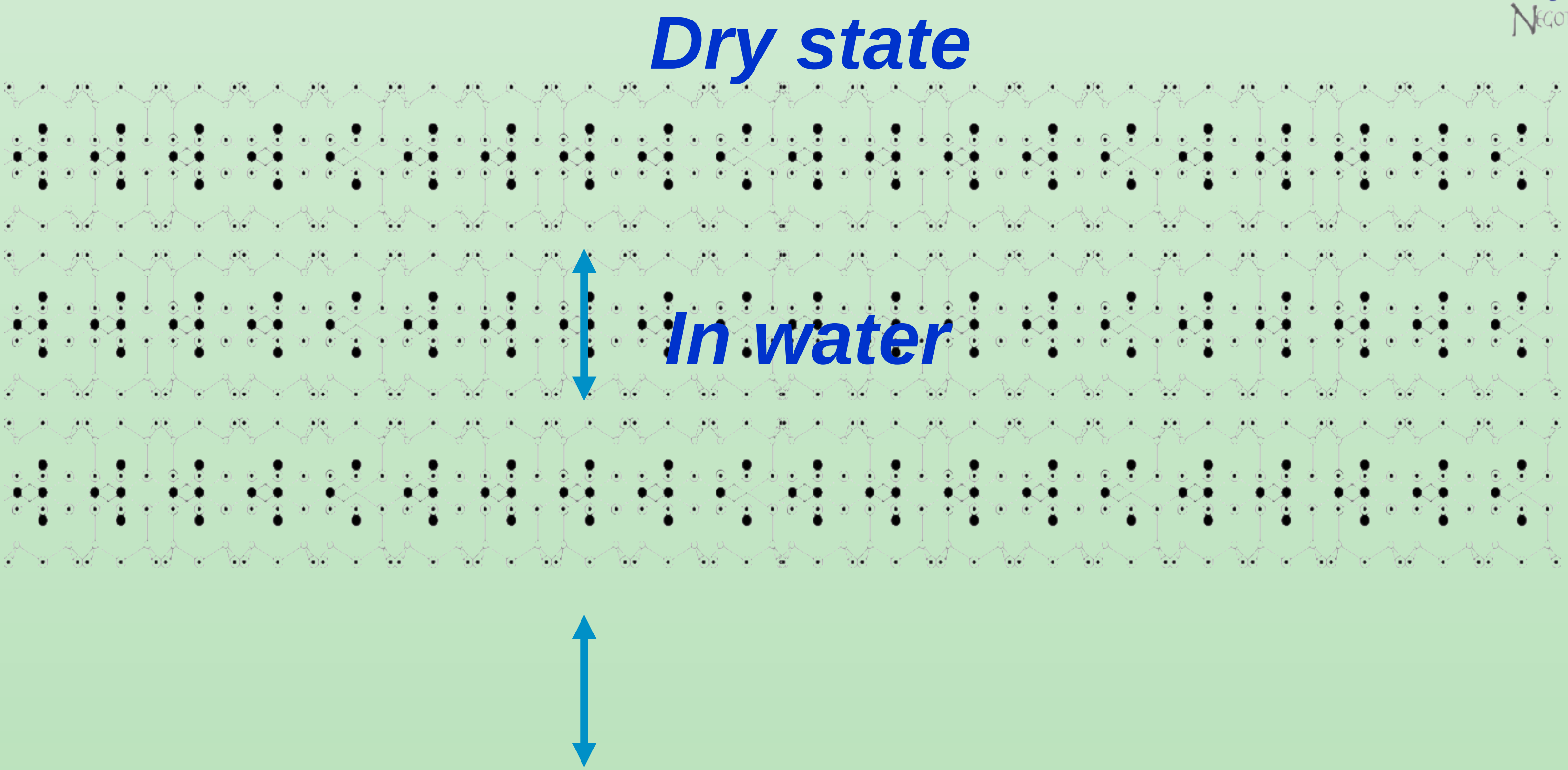


Sepiolite

Electrical charge

- Exchange of Aluminium by other metals or silicon in the crystal structure gives a negative charge on the surface of the sheets (charge deficit)
- In presence of water this charge develops and the particles will separate
- The superficial charge depends on the amount of exchange of Aluminium, the replacing elements as well as counter-cations on the surface of the clay

Phyllosilicates



Clay particles in water

- Automatic separation particles due to negative surface charge > no agglomeration
- Hardly any affinity for textile substrates (negative)
- Settling is extremely slow
- In water the total surface becomes available for the adsorption of organic material as well as metal ions.

Particle sizes of „soil“

- Clays: size of approx. **0,01-2 microns**, can have impurities of a larger size
- Impurities can be silt, or other clays and/or quartz species
- **Some** clays have **nano – surface** size
- The thickness of most clay particles is only around **1 nano-meter**
- The total surface of a clay in water lies between **190-800 m^2/g** of clay

Functions of clays in nature

- Sedimentary clays are essential for the fertility of the soil
- Clays and silt adsorb metal ions
- Clays adsorb also organic matter
- quartz and sand do not have any charge, rain would easily wash plant nutrition away!
- Flooding rivers containing loaded sediments are/were responsible for fertilization of the SOIL!
- *For textile applications these are interesting properties*

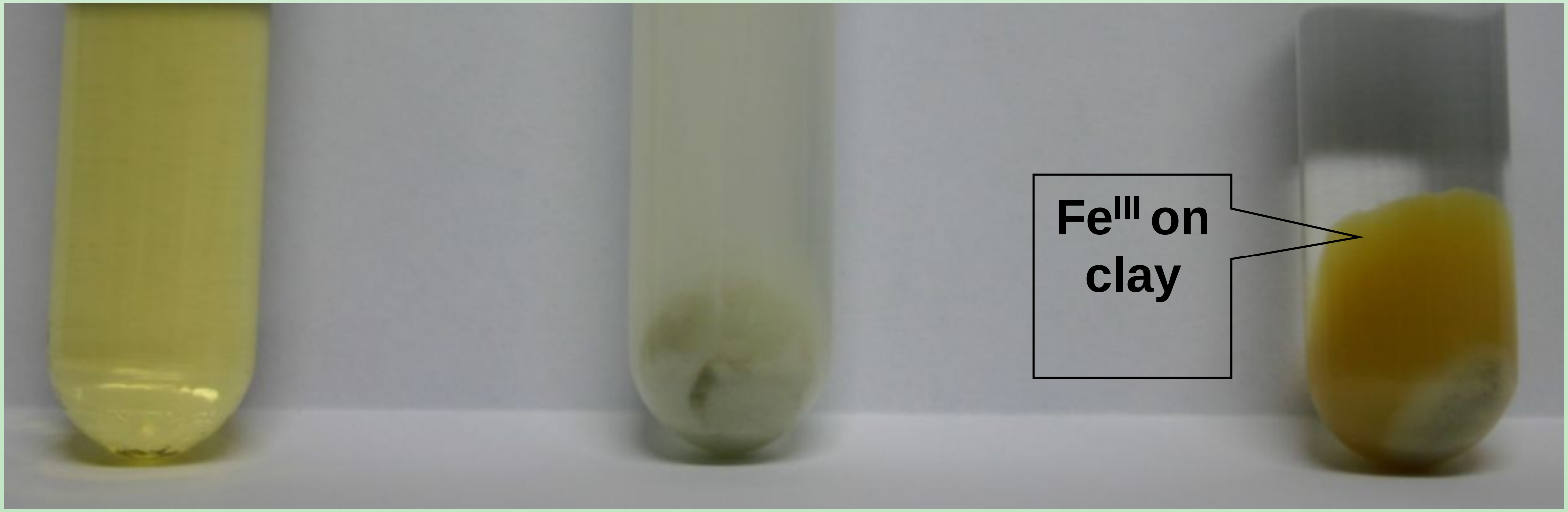
Textile applications

- Sedimentary clays are crude and contain quartz, and inorganic and organic impurities
- For modern processing, interesting clays come from transformed volcanic ash deposits
- For textile applications preferably in their purest form
- Meanwhile many practical experiences in bleaching and scouring processes have been made
- Applications in the dye bath
- Prevention of deposits in a number of applications
- Many other possibilities

The idea is not so new!!!!

For thousands of years and still today, women successfully wash in rivers, using the river water and…… clay present in the river beds!

Bleaching, Fe^{III} -ion elimination

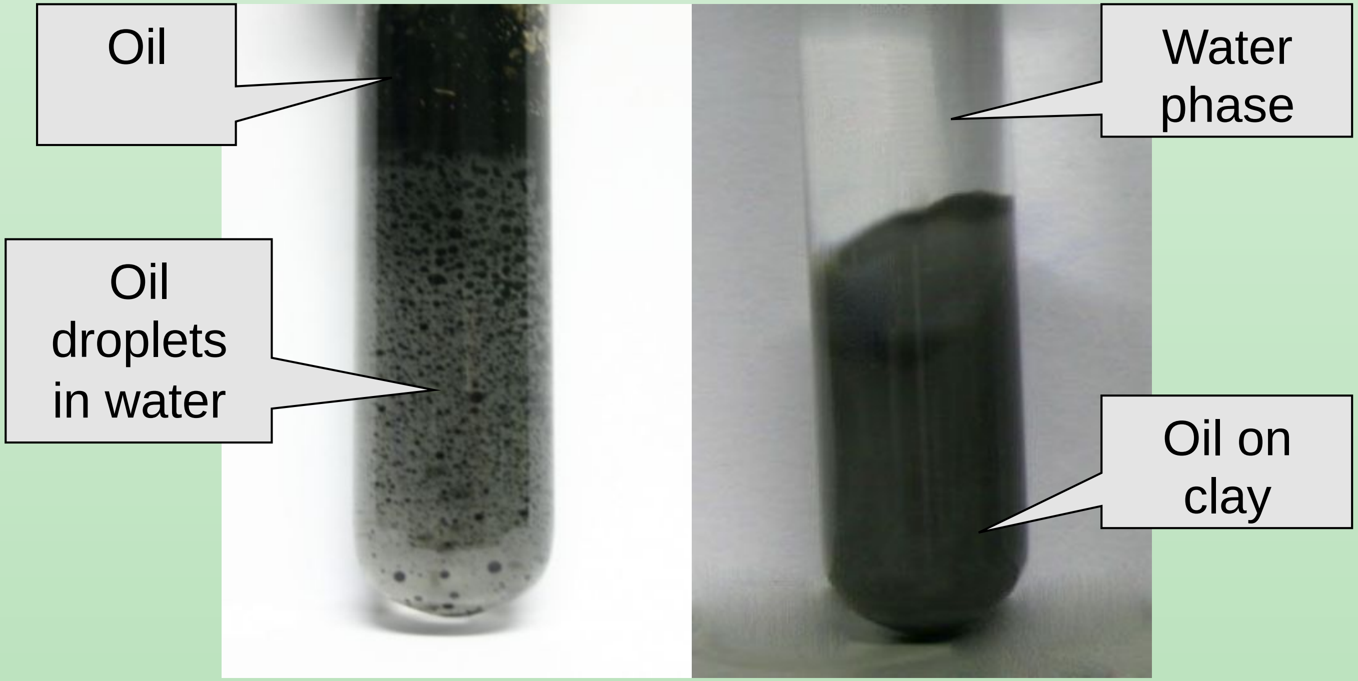


Fe^{III} Chloride **Clay** **Fe^{III}-clay**

(after separation by centrifugation)

Clays show excellent stabilizing properties in peroxide bleaching and adsorb impurities as well

Elimination of oils



in water **in water/clay** *(after centrifugation)*

This performance is the central part of clay based scouring agents

Non-ionic surfactants

Weaknesses of non-ionics

- Above cloud point lower efficiency
  > emulsion break-down
- Limitations because of foam
  > low foaming > low cloud point
- Limited rinsing means take-over in next process step > especially on short-liquor-ratio machines
  Risk of breaking emulsions and deposits on fabric and machines

Clays as alternative

Interestingly the clays are adsorbing at all temperatures and at all conditions

There is no cloud point dependency for clays, absorbency is not influenced by pH, temperature, presence of electrolytes

Very good results in a wide range of industrial applications

Control of crystallization

Many years of practical experience showed that, by using clay based products, preparation and dyeing equipment remained much cleaner.

It was also proved in practice that:

- Scaling of Calcium Carbonate and Calcium Silicate could be reduced on fabrics and machines
- Dyestuff re-crystallization (spots) is diminished
- **Deposits of PES-oligomers could substantially be reduced**

>>>> further investigations for oligomer deposits

Polyester oligomers

- Oligomers are formed during production of PET-polymer (ester interchange reaction), mostly as **cyclic trimers**
- Quantity depend on **quality of polyester**
- Monomers and small agglomerates are **entrapped** in the polymer structure of the fibre
- Oligomers are liberated **during dyeing** at high temperatures
- **Migration to fibre surface** > partly dissolved in the dye bath > partly crystallizing on fibre surface

Determining release factors

- Quality of PET-fibre (up to 4% of trimers)
- Orientation of PET-polymers
- Increasing amounts of oligomers with:
  - Prolonged dyeing times, e.g. slow diffusing dyes
  - Increased dyeing temperatures, dark shades + slow diffusing dyes
  - The use of carriers/diffusing accelerators
  - Type of dyestuff and amount of dye

Formation of trimer crystals

- Migration of oligomers to the surface of the fibre
- Very low solubility in water at dyeing temperature (130-135ºC)
- Homogeneous and heterogeneous nucleation (e.g. on trimers and on dyestuff particles) and subsequent crystal growth
- Formation of bigger crystals in the dye bath and on fibre surface, filtration and redeposition

Lab-investigations

A number of clays was investigated. > one example on PES yarn:
Apparatus: Tinto-Lab, 6% Black, 60 min at 135ºC, slow cooling
Methanol: surface oligomers > DMC: total amount of oligomers

Material	Methanol extraction	Di-chloromethane extraction
Greige PET-yarn	0,07%	1,96%
Dyed without auxiliaries	0,96%	1,15%
Dyed with Formulation 9743	0,03%	1,07%

Conclusions

- Most clays had a positive effect on oligomer re-deposition
- Formulation nr. 9743 was the best of them, now called CERRIOSTAR AO
- Industrial trials were started with excellent results in respect of visible oligomer redeposition of fabrics (see next slide)
- Machines had substantially less oligomer deposits (as well as less dye and other residues)
- Oligomer control on dyed goods: > <u>reduction of oligomers</u> but not as good as lab (filtration > density?)
- <u>Oligomers, which could be detected, are **not visible**</u>

Prevention of oligomer deposits

Dyeings with (top) and without (below) CERRIOSTAR AO (formerly Formulation 9743) (inside of the beam)

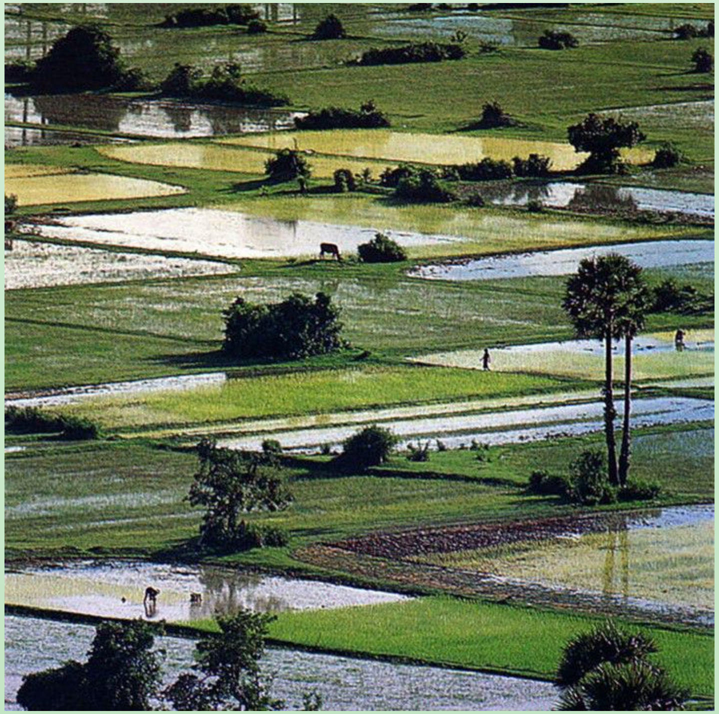
Prevention of oligomer deposits

To give some idea about machine soiling (and possible impact on subsequent dyeings) >

Beam dyeing equipment with severe PES-oligomer deposits

Conclusions

- The surface activity of clays is not only effective for metal control during peroxide bleaching
- And not only effective as soil absorbent in textile processing
- But can **control crystallization** and can at least reduce substantially crystal size of a number of substances
- Interestingly also **PET-Oligomers**
- After Blowing-out-equipment, alkaline-PES-dyeing and numerous dispersing agents to overcome oligomers, <u>**a big step forwards has now been made**</u>



Green *“non-chemical”* Technology

Products based on natural minerals, which have been formed

over a period of <u>3,8 Billions of years</u>

thank you