A CHEMICAL SUBSTITUTION STUDY FOR A WET PROCESSING TEXTILE MILL IN TURKEY

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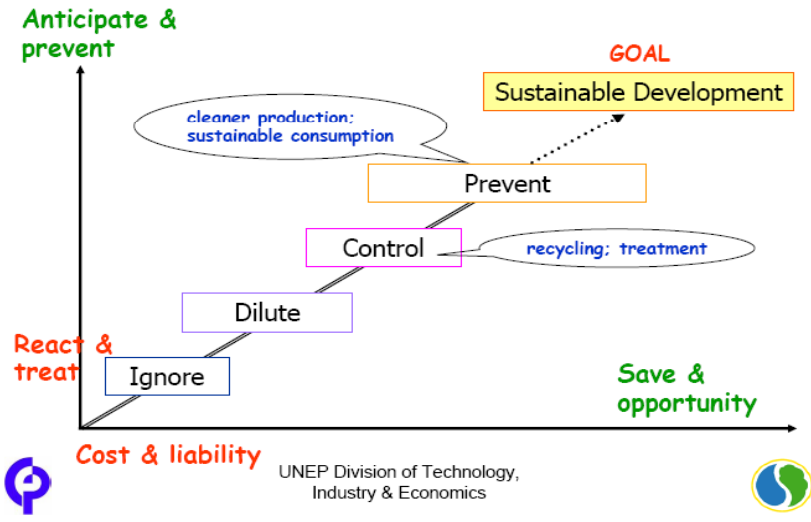
"Given existing technology and products, for all over six billion people on the planet to live like the **average American**,

we would require the equivalent of **three planet Earths** to provide the material, create the energy and dispose of the waste.

Environmental Management Evolutionary "Ladder"



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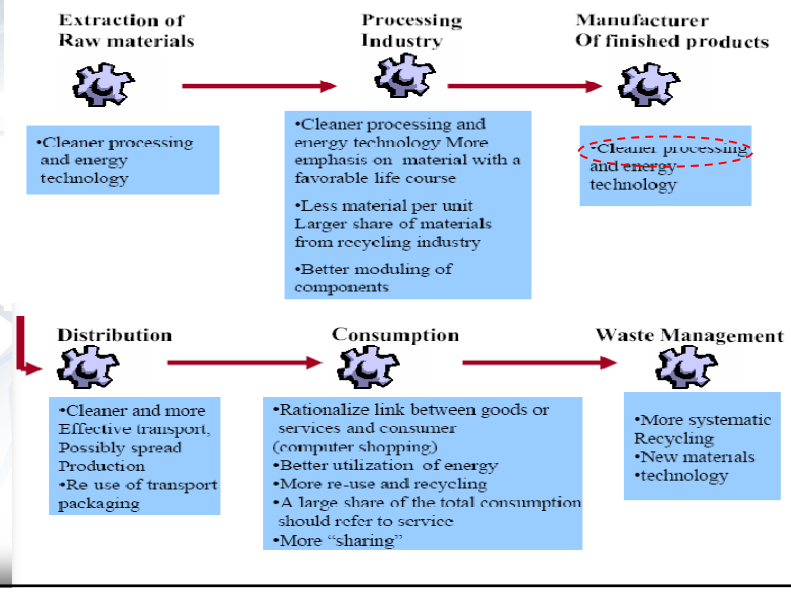
Strategies to improve resource productivity during the life cycle of a product



MAIN TOOLS OF CLEANER PROCESSING (OR SUSTAINABLE PRODUCTION)

- Good Housekeeping
- Waste Reduction Audit
- Environmental Compliance Audit
- Life Cycle Analysis
- Environmental Performance Assessment
- Environmental Impact Assessment
- **Chemical Substitution Assessment**
- Risk Audit
- Industrial Ecology
- Design for Environment
- Green procurement
- Green Supply Chain Management

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Textile Manufacturing is one of the Largest Industrial Producers of Wastewater

➔**Water Use: 95-400 l/kg fabric (SRK, 1993; PRG, 1998; Bar. & Buck., 2000; USEPA)**

➔**Textile Sector Notebook prepared by USEPA indicating that Textile manufacturing is a "Chemically Intensive Process",**

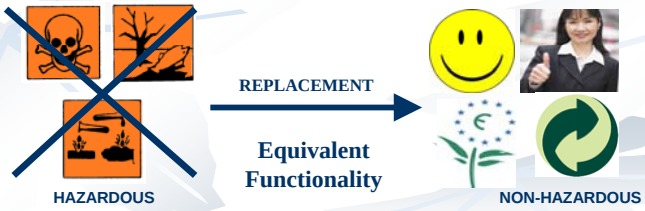
➔ **"Pollution Prevention Studies in The Textile Wet Processing Industry" by Hendrickx and Boardman showing that "The total quantity of chemicals used in textile mills varies from *10% to over 100%* of the weight of the cloth"**



DEFINITION of CHEMICAL SUBSTITUTION

Chemical Substitution defined as;

"the replacement or reduction of hazardous substances in products and processes by less hazardous or non-hazardous substances" (NYSDEC, 1999; Lohse et al., 2003; Thorpe, 2005; Oosterhuis, 2006)



Chemical Substitution in Textile Mills (1/3)

➔Substitution of the harmful substances is an option to reduce the environmental impact of a process. [EU IPPC, BAT Ref. Document]

➔A primary focus for pollution prevention should be on Substituting Less-Polluting Chemicals

➔Chemical Substitution can eliminate chemical waste and the need for costly pollution control equipment

Chemical Substitution in Textile Mills (2/3)

➔ **Case Study 1**

A textile mill performing Dyeing, Finishing & Printing Processes substituted Carbon Dioxide Gas for Sulphuric Acid used for neutralization of high alkaline process water before reaching WWTP

Total Investment: 210 000 € & Payback Period: 4 years

[Regional Activity Centre for Cleaner Production (RAC/CP), 2002]

Chemical Substitution in Textile Mills (3/3)

➔ **Case Study 2**

A textile mill manufacturing knit fabrics performed a waste reduction program (including paper and metal recycling, solid waste reduction, upgrading WWTP and Chemical Substitution)

Substituting pollutant chemicals and upgrading the WWTP, the company reduced BOD, COD, and TSS by 50, 24 and 60 percent, respectively. [North Carolina Department of Environment and Natural Sources, 1995, Case Study]

CHEMICAL SUBSTITUTION EXAMPLES in TEXTILE INDUSTRY

Substitution is common way of PP
- Substitution of

- **Sizing agents** (Jones, 1973; NCOWR, 1993; Hendrickx & Boardman, 1995; EC, 2003)
- **Surfactants** (Smith, 1989b)
- **Urea** (Provost, 1992)
- **Solvent** (Smith & Whisnant, 1988; NCDEHNR, 1995; USEPA, 1995; DeSimone, 2002)
- **Acid** (RAC/CP, 2002)
- **Reducing agents** (Snowden & Swan, 1995)

Textile Industry in Turkey

The textile sector is one of the vital sectors in Turkey's Economy. Turkey is;

➔The World's Sixth Largest Producer of Cotton

➔The Fifth Largest Cotton Consumer

➔The Fifth Largest Woolen Producer

➔In Top Ten Producers of Synthetic Yarns

According to data referring to the period 1999-2000

[Regional Activity Centre for Cleaner Production (RAC/CP), "Mediterranean Action Plan: Pollution Prevention in the Textile Industry within the Mediterranean Region", September 2002]

THE TEXTILE MILL INVESTIGATED

The Mill Studied;

- **One of the Major Textile Mills in Turkey**
- **Capacity of 20.000 Tons of Ring Yarn & 40 Mil. Meter of Denim Fabric per Year**
- **Including Dry & Wet Processes:**

Cotton Fiber Production → **Dyeing** → **Sizing** → **Finishing**

THE TEXTILE MILL INVESTIGATED

- **The production is 24 hours a day & 3 shifts/day**
- **The water consumption of 3500-5000 m^3/day**
- **Chemical consumption of 1000 ton/month**
- **Over 100 chemicals used**
- **It has own WWTP and Co-generation Units**

METHODOLOGY

Chemical Screening

(Chemical Species, Process Recipes, Chemicals' Consumption Levels, Chemicals' MSDS)

↓

Literature and Manufacturer's Database Research and Chemical Suggestion of the Suppliers

(Alternative Chemicals Determined)

↓

Experimental Analysis

(Biodegradability Tests)

↓

Evaluation of Substitutions

PROBLEMATIC CHEMICALS & THEIR ALTERNATIVES

On the Ecological Side, a Textile Chemical Should Have;

- **High Biodegradability**
- **Less Toxicity**
- **Less Nitrogen (N) & Phosphorus (P) content**

(EC, 2003)

A. DISPERSANTS

Dispersants are additives in the dyeing processes to maintain the stability of the dispersion throughout the dyeing process

Dispersants mainly consist of

- **Naphthalene sulphonate-formaldehyde products**
- **Lignin sulphonates**

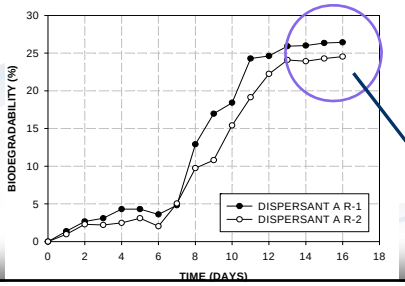
ENVIRONMENTAL PROBLEMS about USE of DISPERSANTS

- **Dispersants are not toxic to aquatic life,**
- **Poorly biodegradable**
- **Especially for the chemicals having high COD values, low biodegradability can be very significant**

PROBLEMATIC DISPERSANT USED in the PRODUCTION

The "Dispersant A" is used as dispersant additives in the dyeing processes in the factory

- **Dispersant A**
  - **Naphthalene sulfonic acid formaldehyde poly-condensate**
  - **Consumption of 1500 kg/month**



LOW BIODEGREDABILITY

MSDS Value : 30-70%

Experimental Value : ~ 25%

ALTERNATIVE CHEMICALS

The supplier of the "Dispersant A" suggested Dispersant A* having Biodegradability of 70-100%

And supplier also indicated that this alternative can have negative effects on denim product quality

This substitution option was dropped due to the non-existence of better alternatives

SULPHUR DYES

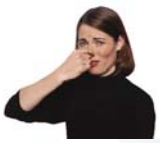
- **Sulphur dyestuffs are of great importance world-wide in dyeing cotton**
- **Sulphur dyes are insoluble in water and they need to be converted to be water-soluble and have a high affinity for the fiber**
- **Before dyeing, they have to be reduced with sodium sulphide in alkaline conditions**

ENVIRONMENTAL PROBLEMS about the USE of SULPHUR DYES

Excess of Sulphide Responsible for;

Aquatic Toxicity

Odor Problems



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PROBLEMATIC SULPHUR DYES USED in the PRODUCTION

There are three dyestuffs with high sulphide content used in the dyeing process;

Dyestuff	Sulphide Content (%)
Sulphur Dye A	5-10
Sulphur Dye B	12-15
Sulphur Dye C	12-15

PROBLEMATIC SULPHUR DYES USED in the PRODUCTION

Two Ways of Sulphide Load to WWTP

Wasted Sulphide **Unfixed Sulphide**

Significant amount of dyestuffs and auxiliaries are wasted after each dyeing operation

Dyestuff	Amount Wasted (kg/month)	Sulphide Wasted (kg/month)
Sulphur Dye A	1000	50-100
Sulphur Dye B	22	2.6-3.3
Sulphur Dye C	110	13.2-16.5
TOTAL	**1132**	**65.8-119.8**

PROBLEMATIC SULPHUR DYES USED in the PRODUCTION

Unfixed Sulphide

Sulphur Dyes have 60-90% Fixation (EC, 2003)

Consequently 10-40% of Dyes Discharged to WWTP

Sulphur Dyestuff	Consumption Amount (kg/month)	Sulphide content (%)	Amount of Unfixed Dyestuff (kg/month)	Amount of Unfixed Sulphide (kg/month)
A	37500	5-10	3750-15000	188-1500
B	800	12-15	80-320	10-48
C	3900	12-15	390-1560	47-234
TOTAL	**42200**		**4220-16880**	**245-1782**

ALTERNATIVE CHEMICAL

The Factory Ordered One New Dyestuff With Lower Sulphide Content (Sulphide Content 1-4%) for Sulphur Dye A

New Projection for Wasted Sulphide

Sulphur Dyestuff	Amount of Sulphur Dyestuff Wasted (kg/month)	Sulphide Content (%)	Sulphide Wasted* (kg/month)
A*	1000	1-3	10-30
B (No Use)	-	-	-
C (No Substitute)	110	12-15	13.2-16.5
TOTAL after Substitution	**1110**		**23.2-46.5**
TOTAL before Substitution	**1132**		**65.8-119.8**
Reduction in the Wasted Sulphide (%) 61-65			

*Calculated on the basis of Sulphide content of the sulphur dyestuffs

ALTERNATIVE CHEMICAL

New Projection for Unfixed Sulphide

Sulphur Dyestuff	Consumption Amount (kg/month)	Sulphide content (%)	Amount of Unfixed Dyestuff* (kg/month)	Amount of Unfixed Sulphide** (kg/month)
A*	37500	1-3	3750-15000	4-450
B (No Use)	-	-	-	-
C (No Substitute)	3900	12-15	390-1560	47-234
TOTAL after Subs.	**41400**		**4140-16560**	**51-684**
TOTAL before Subs.	**42200**		**4220-16880**	**245-1782**
Reduction in the Unfixed Sulphide (%) 62-79				

* Calculated on the basis of sulphur dyestuff fixation rate
** Calculated on the basis of sulphide content of the sulphur dyestuffs

RESULT of the SUBSTITUTION

Sulphide Discharged to WWTP

Before Substitution
310-1900 kg/month

After Substitution
74-731 kg/month

Reduction
Up To 76%

C. EASY-CARE FINISHING AGENT

- **Easy-care finishing increase the crease recovery and/or dimensional stability of the fabrics**
- **Easy-care finishing agents are urea, melamine, cyclic urea derivatives and Formaldehyde**

ENVIRONMENTAL PROBLEMS about the USE of FORMALDEHYDE BASED EASY-CARE AGENTS

- **Formaldehyde-based cross-linking agents may release free formaldehyde**
- **Carcinogenic and is a Threat To The Workforce (especially during cutting operations)**
- **Free formaldehyde potential Risk for the Consumer**
- **The European Eco-label scheme sets a threshold of 30 ppm (EC, 2003)**

PROBLEMATIC FORMALDEHYDE BASED EASY-CARE AGENTS USED in the PRODUCTION

The "Easy-care Agent A" is used for easy-care chemical for the finishing processes

Agent A

- **Formaldehyde based**
- **Consumption of 840 kg/month**
- **Containing 0.1-1 % formaldehyde on weight base**
- **Not a low-formaldehyde chemical (EC, 2003)**

The denim products contains less than 25 ppm Formaldehyde content

The possible risk is Threat To The Workforce during cutting process

ALTERNATIVE CHEMICAL

- **Low-formaldehyde or even formaldehyde-free products are the alternatives**
- **The supplier suggested a Formaldehyde-free chemical**
- **The Firm States that This Substitute is 3 times Expensive than "Formaldehyde A"**

D. COMPLEXING AGENTS

- **Complexing agents mask hardening alkaline-earth cations and trasition-metal ions in aqueous solutions in order to *Eliminate Their Damaging Effect*, especially in pretreatment processes and also during dyeing operations.**

Typical agents;

- **Polyphosphates (e.g. tripolyphosphate)**
- **Phosphates (e.g. 1- hydroxyethane 1,1-diphosphonic acid)**
- **Amino carboxylic acid (e.g. EDTA, DTPA, and NTA)**

ENVIRONMENTAL PROBLEMS about the USE of COMPLEXING AGENTS

- **Use of these substances arise from their N and P content**
- **They have often low biodegradability/bioeliminability**
- **Their ability to form stable complexes with metals**

PROBLEMATIC COMPLEXING AGENTS USED in the PRODUCTION

Complexing Agent A
- Blend of organic compounds
- Consumption of 1100 kg/month
- Poorly biodegradable

Complexing Agent B
- Phosphonic Acid
- Consumption of 1000 kg/month
- Biodegradability is low (20-70%)

These Two Used in Finishing Line

Complexing Agent C
- EDTA Derivative
- Consumption of 4000 kg/month
- Potentially biodegradable
- Difficult to eliminate in WWTP

This One Used in Dyeing Operations

ALTERNATIVE CHEMICALS

Supplier suggested 3 alternative Complexing Agents

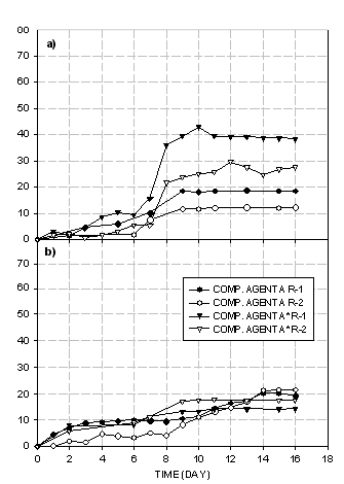
Complexing Agent A* for A

Complexing Agent B* for B

Complexing Agent C* for C

RESULTS of the PROJECTED SUBSTITUTIONS

Both A & A* are LOW BIODEGRADABLE (MSDS val.)



Low and High Concentrations of the Chemicals A and A´ tested

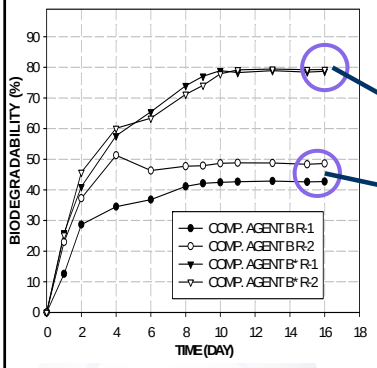
Chemical	Concentration in the Reactor (ml/l)	Corresponding COD value (mg/l)
A	1,3	455
	2	700
A*	1,5	405
	2,9	783

Biodegradability Data

Chemical	Conc.	Biodegradability (%)
A	LOW	15
	HIGH	21
A*	LOW	34
	HIGH	15

RESULTS of the PROJECTED SUBSTITUTIONS

Complexing Agent B* More Biodegradable than B (MSDS Val.)



Chemical	COD Value of Chemical (mg/ml)	Concentration of Chemical in the Reactor (ml/l)	Corresponding COD Value in the Reactor (mg/l)
B	100	8.75	875
B*	110	7.1	781

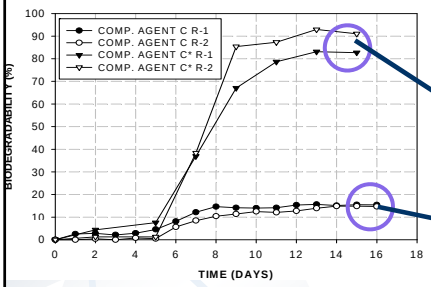
Chemical	Biodegradability * (%)
B	46
B*	79

*Average of parallel runs, R-1 and R-2

some modifications in the finishing processes will be necessary
the implementation of the new chemical needs initial financial supply
cost benefit study should be conducted

RESULTS of the SUBSTITUTION of COMPLEXING AGENT C* for C

Complexing Agent C* More Biodegradable than C (MSDS Val.)



Chemical	Concentration in the Reactor (g/l)	Corresponding COD value (mg/l)
C	0.5	650
C*	1	525

Chemical	Biodegradability * (%)
C	15
C*	87

*Average of parallel runs, R-1 and R-2

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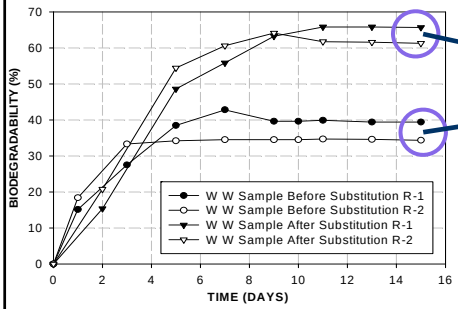
RESULTS of the SUBSTITUTION of COMPLEXING AGENT C* for C

Biodegradability Evaluation of WW Samples Before & After Chemical Substitution

Samples Collected from the the first post-washing tank just after the dye bath



WW sample	Biodegradability * (%)
Before Subs.	38
After Subs.	64

*Average of parallel runs, R-1 and R-2

The COD concentration of the wastewater sample was dropped to 840 from 2000 mg/l. Due to the COD val. of the Chemicals

3100 kg of COD load to the WWTP was prevented

CONCLUSIONS

- **Totally, 8 out of 128 chemicals were identified as problematic. Consumption levels of the Problematic ones 50 tons/month** (represents 5% of total cons.)
- **Substitution of Dyestuff A* reduces sulphide discharged to WWTP up to 76%** (this substitution decreases the inhibition risk on microorganisms in the WWTP)
- **Substitution of Complexing Agent C* for C has led to enhancement of the biodegradability of wastewater samples by at least 25%** (from 38 to 64%)
- **Substitution of Complexing Agent C* for C prevents the 3100 kg of COD load to WWTP**

THANK YOU FOR YOUR ATTENTION

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