

Polymer Deformation



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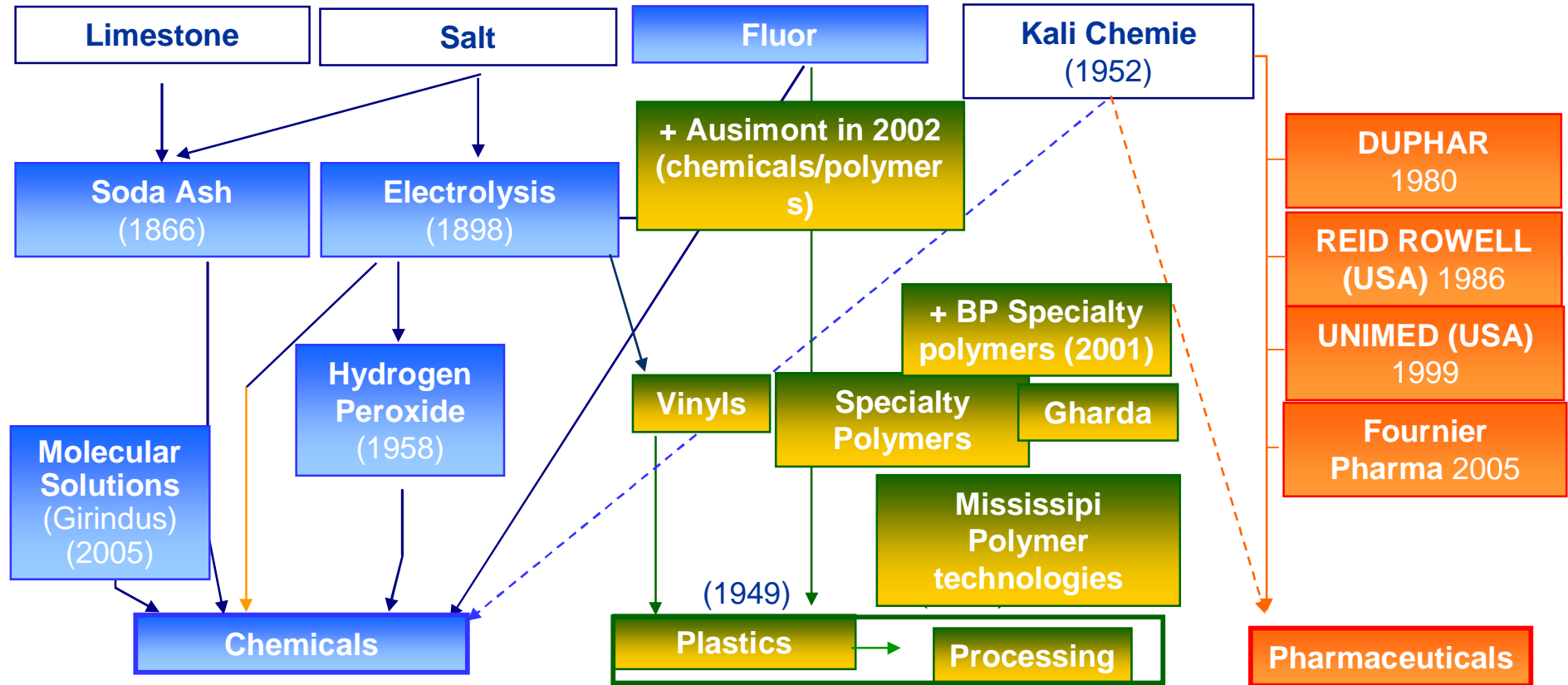
Additives and Processing Aids for polymer Conference
Sint-Martens-Latem (Gent) - October 22nd 2008





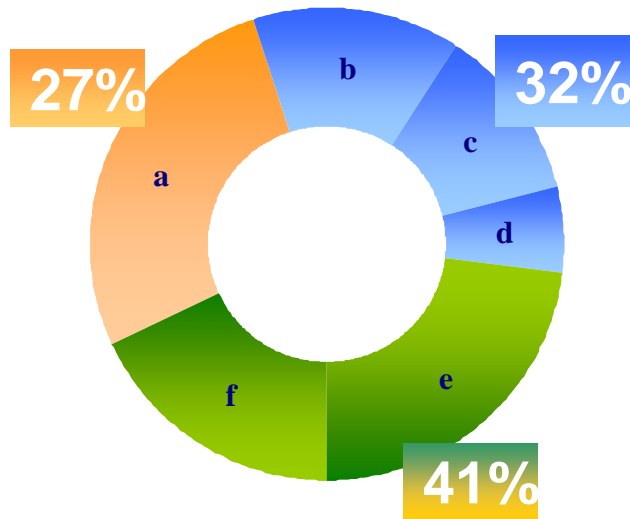
- ◆ **Presentation of the Solvay Group**
- ◆ **General approach**
- ◆ **Complete deformation of a PVC decorative sheet**
- ◆ **Determination of additive in polyolefins**
- ◆ **General conclusion**

Solvay group

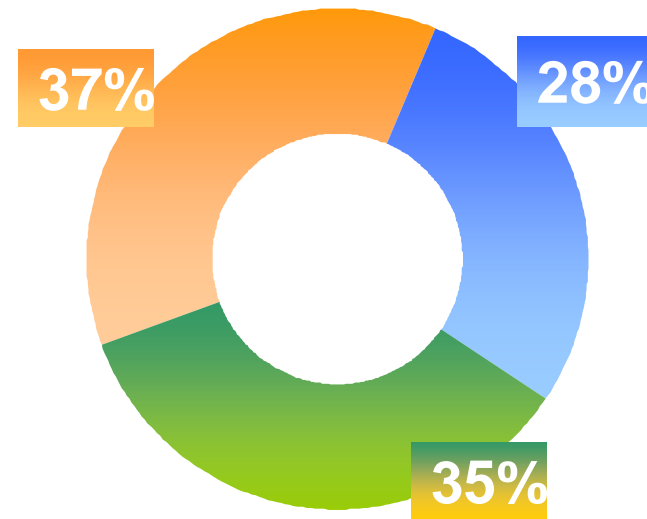


Three profitable & cash generating sectors
with specific strategy for growth

In % of 2007 Sales¹



In % of 2007 REBIT²








- **Pharmaceuticals (a)**
- **Chemicals** : (b) Minerals, (c) Electrochemistry and Fluor Products, (d) Oxygen
- **Plastics** : (e) Vinyls, (f) Specialty Polymers and Inergy Automotive Systems

¹ Total 2007 Sales = EUR 9,572 M

² Total 2007 REBIT = EUR 1,192 M, including also "Corporate and Business Support" of EUR -51 M



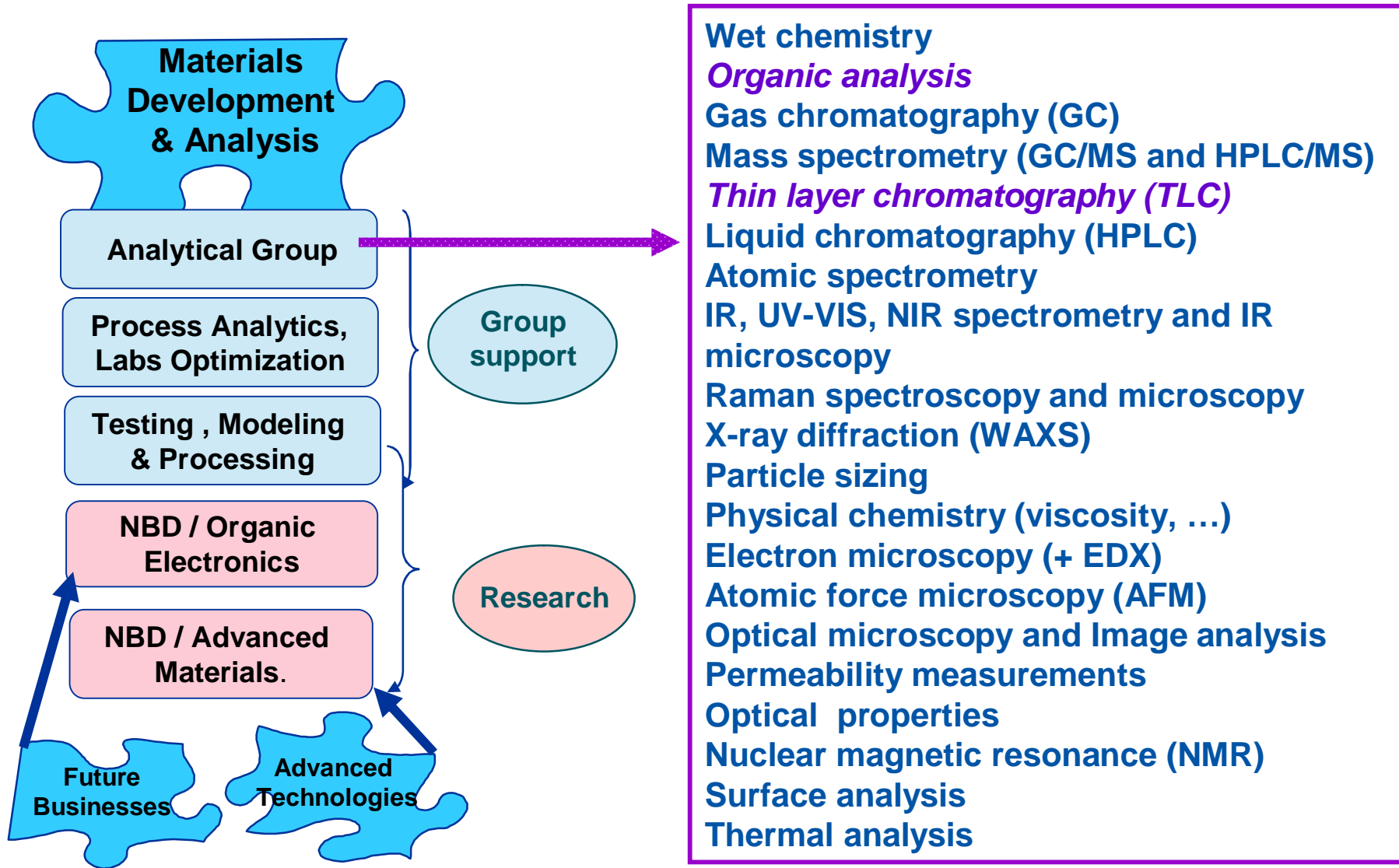
Solvay Research & Technology of NOH

Business Partner	SOLVAY Chemicals Sector Competence Centers BSC	PEPTISYNTHA Peptides	SOLVIN PVC / PVDC BASF 25%	INERGY Fuel Systems IVC PLASTIC OMNIUM 50%	INEOS Polyethylene PE-HD / PE-LD Polypropylene INEOS 100%
					

And three start-up ...



Solvay group

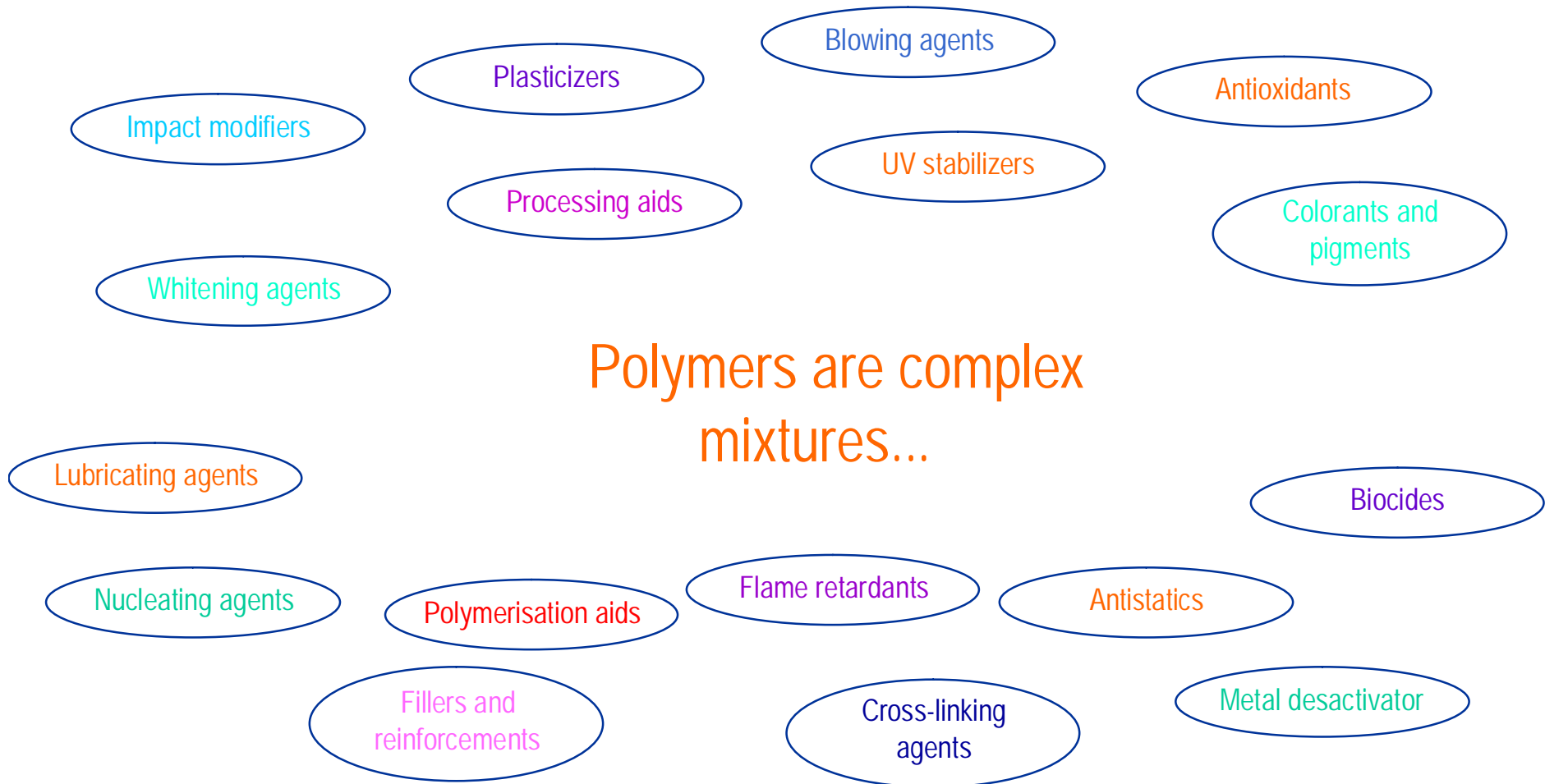


◆ Types of polymers

- Polyvinyls
 - PVC, copolymers
 - PVDC, copolymers
 - PVDF, copolymers
- Polyamides
- Polysulfones
- Polystyrene
- Polyesters
 - PET
 - Poly(meth)acrylates
- Polyolefins (PO)
 - PP
 - PE
 - Grafted PO (maleic anhydride)
- ...



General approach



◆ Discussion with the customer

- what is the purpose of the request, the problem ?
- what kind of information is required ?

◆ Preliminary analysis : general information

- X-ray Fluorescence, IR spectrometry, optical microscopy, ...

◆ Sample preparation

- solvent separation (fractionation)
- solvent extraction
- separation of (multi)layers (mechanical : milling machine, minimum thickness is $\sim 75 \mu\text{m}$)

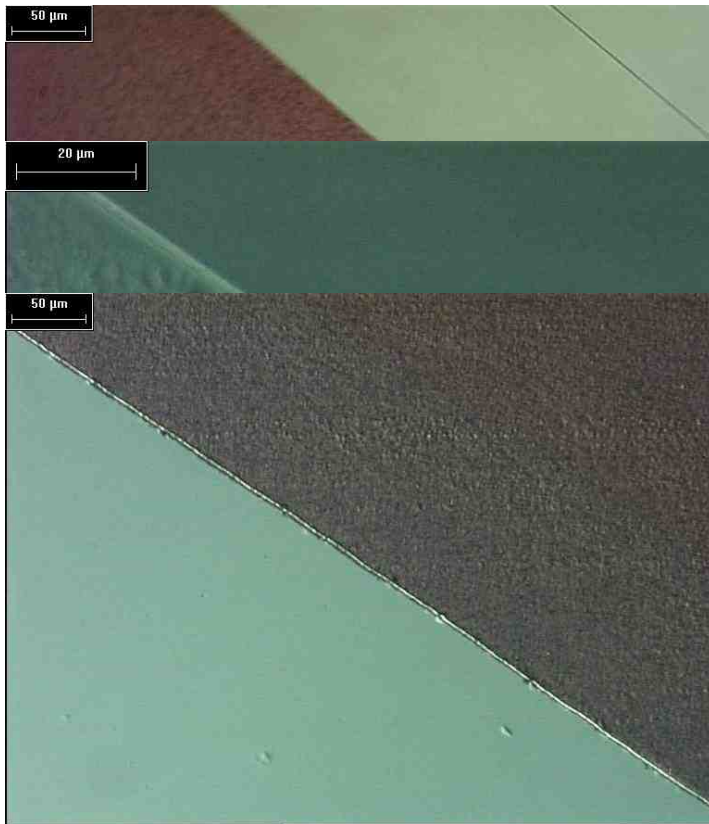


Complete reformulation of
a PVC decorative sheet



Complete deformation of a PVC decorative sheet

◆ Analysis by optical microscopy



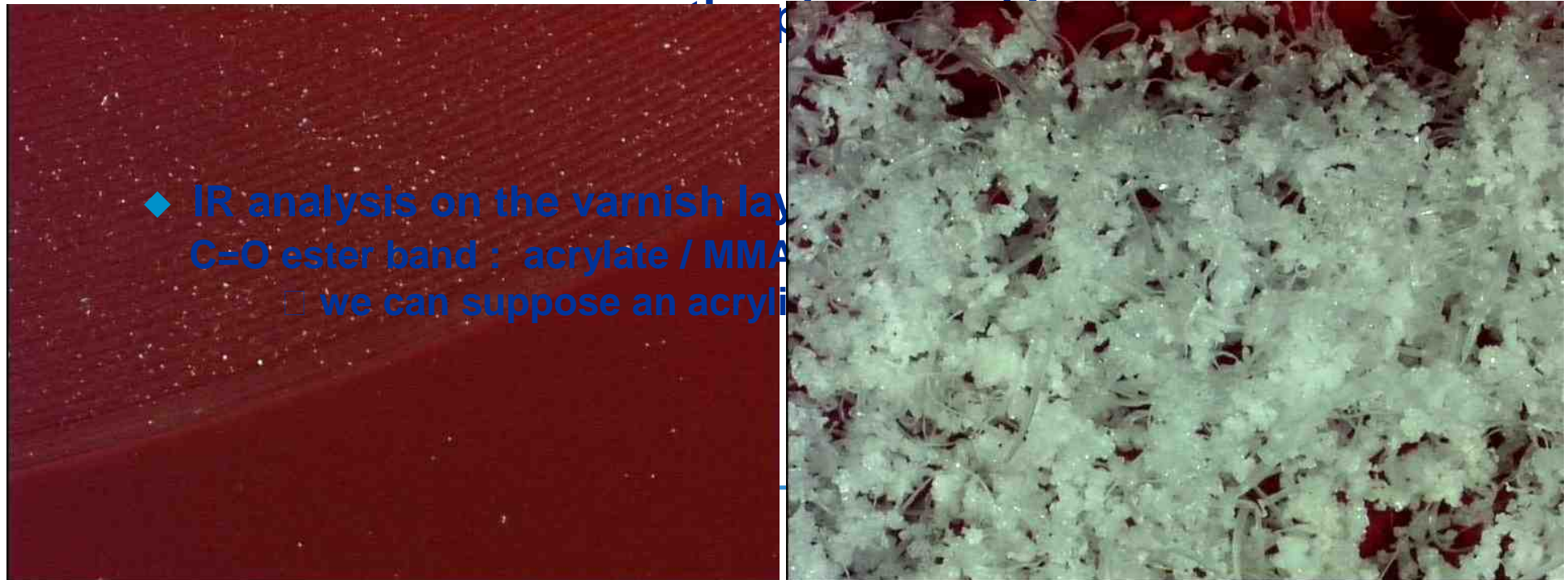
main layers : transparent 145 µm
 pigmented 178 µm
 pigmented 138 µm

laquer (varnish) layer ~1 µm

primer 1 µm

Complete deformation of a PVC decorative sheet

- ◆ **After discussion, agreement on further analysis :**
 - examination by IR spectroscopy (ATR) of the varnish layer
 - analysis of the composition of the transparent layer
 - analysis of the composition of the pigmented layers together
- **after milling, we recover the transparent layer**

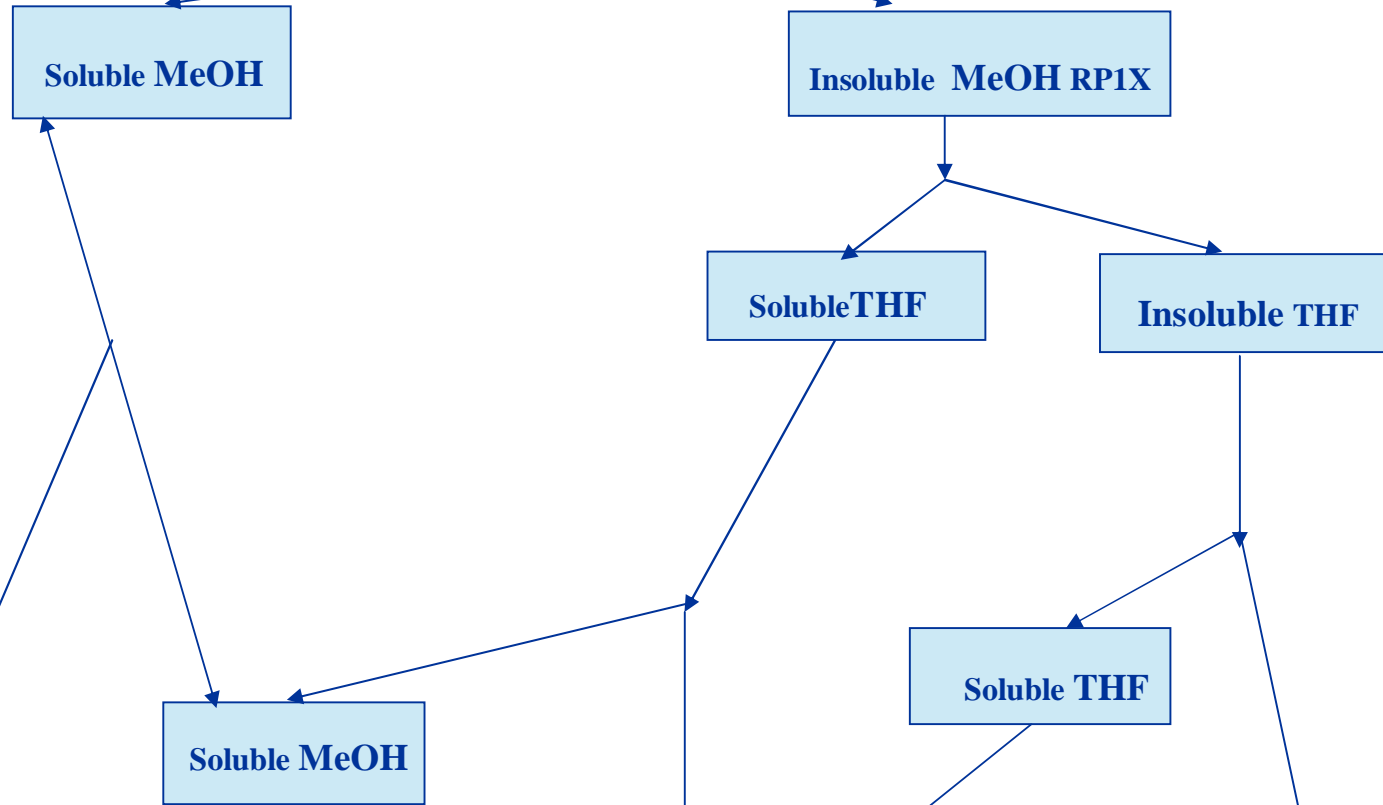


◆ Examination by X-ray fluorescence

Elements	% weight	
	Pigmented intermediate layer	Pigmented bottom layer
Na	0.01	0.06
Al	0.01	0.04
<u>Si</u>	< 0.01	1.7
P	< 0.01	0.03
<u>S</u>	0.3	0.3
Cl	47	52
K		0.01
Ca	0.04	0.05
<u>Ti</u>	0.2	0.3
Fe	0.01	
<u>Sn</u>	0.2	0.2
Ba	nd	nd

Polyvinyl
sample **de**formulation

*Fractionation
general scheme*



<p>Insoluble ES</p> <p><i>Surfactants, blowing agent, ... IR, MS</i></p>	<p>Soluble ES</p> <p><i>Plasticizers TLC, GC, GC-MS</i></p>	<p>Insoluble MeOH RP2X</p> <p><i>Polymers (not cross-linked) Polymeric plasticizer IR, NMR</i></p>	<p>Insoluble THF</p> <p><i>Fillers, pigments Cross-linked polymers IR, XRD</i></p>
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Complete reformulation of a PVC decorative sheet

	% weight	
	Transparent layer	Pigmented layers
- Polymeric phase not cross-linked; NMR 1H mainly shows the presence of PVC and a small amount of polymeric units MMA and styrene. Possible presence of units EA and/or BA.	92	91

	% molar	
	Transparent layer	Pigmented layers
. VC1 unit	99.2	98.8
. MMA unit	0.6	0.8
. Styrene unit	0.1	0.4

the K-value of polymeric phase for transparent layer : 60.3
 pigmented layers : 60.5 - 60.5



Complete deformation of a PVC decorative sheet

	% weight	
	Trans. layer	Pigm. layer
Fraction of additives soluble in methanol analysed by TLC	2.4	3.4
. mainly epoxidized soybean oil	-	+
di and tri oleate of glycerol	+	-
aromatic ester (similar to trimellitate in C ₈)	-	+
tin derivatives of the kind thio tin (for example 17 MOK)	+	+
. presence of oligomers	+	+
fatty acids (oleic ?)	+↑↑	+↓
mono oleate of glycerol	+↑	+↓
. presence in small ^{and/} _{or} very small amount of Irganox 1076	+	+↓
hydrocarbons (paraffins)	+	+↓
esters (adipate ?)	+	+
red colorant	-	+
. possible presence of other(s) component(s) (components of degradation ^{and/} _{or} decomposition of tin derivates, others esters, ...)	+	+



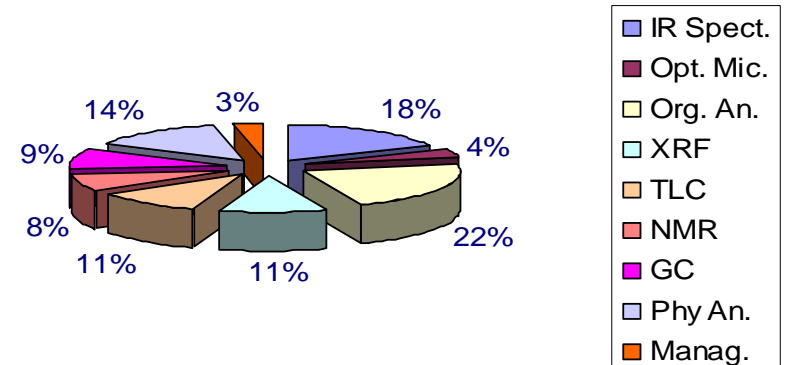
Complete deformation of a PVC decorative sheet

	% weight	
	Trans layer	Pigm. layer
- Insoluble fraction in THF, analyzed by IR	5.3	5.3
. butadiene	+	+
. styrene	+	+
. MMA	+	+
. possible presence of acrylate	+	+
. weak alcohol band ^{and/or} ether ^{and/or} mineral component	-	+
. metallic salt of fatty acid ^{and/or} nitrogen component in weak amount	+	+
. long hydrocarbonated chain	-	+
. mineral component	-	+
. metallic oxide	-	+
. weak C=O amid band	-	+
. possible presence of metallic carbonate	-	+

Complete deformation of a PVC decorative sheet

The sheet can be fully deformed but :

- it is important to have a good communication with the customers (before, during and after the analyses)
- it is necessary to have a good knowledge of the polymers and their "additives" to select the best analytical strategy
- it is a multi-technical approach, which requires a complementary work between the different techniques
- keep in mind a good compromise between cost and delay





Additive determination in polyolefins

Question

Qualitative and quantitative analysis of additives in PP pellets expanded

- ◆ Antioxidants
- ◆ UV absorbers [monomeric and oligomeric (Hals)]
- ◆ Stabilizers
- ◆ Lubricants
- ◆ Antistatics
- ◆ Nucleants
- ◆ Others

◆ Examination by X-ray fluorescence : PO calibration

Elements	mg / kg
<u>Al</u>	48 - 52
Ba	< 1 - < 1
<u>Ca</u>	153 - 152
<u>Cl</u>	99 - 93
Cr	< 1.0 - < 1.0
Fe	9.0 - 9.1
<u>Mg</u>	249 - 239
Na	17 - 13
<u>P</u>	195 - 193
<u>S</u>	108 - 103
<u>Si</u>	1193 - 1184
Ti	2.2 - 2.0
Zn	< 2 - < 2

◆ Qualitative extractions

- ◆ solvents and mixture of solvents
- ◆ temperature (depending on the PO)

◆ Screening by TLC

- ◆ basic screening
- ◆ complementary screening

◆ Quantitative extractions

- ◆ quantification by HPLC, GC, TLC

◆ If necessary, identification by GC-MS, HPLC-MS, TLC preparative – MS/NMR/IR

◆ Basic screening :

- Irgafos 168 (ite form) + 2,4-diterbutyl phenol → antioxidant
- Unknown component 1 (aromatic component)
- Irganox 1010 → antioxidant
- Unknown component(s) 2
- Fatty alcohols
- Irganox MD1024 → antioxidant
- Free fatty acids
- Metallic salts of free fatty acids → antiacid
- Fatty amid (similar to erucamid) → lubricant
- Esters of glycerol (mono and di-esters similar to Atmer 122) → antistatic
- Unknown components 3 (nitrogenated ? ethoxylated ? components such as ethoxylated amid ?) → antistatic
- Other nitrogenated and aromatic unknown component(s) 4 [polar component(s)]

◆ Complementary screening

- Irgafos 168 (ite form) + 2,4-di(terbutyl) phenol → antioxidant
- Tinuvin 326 → UV stabilizer
- Irganox 1010 → antioxidant
- Distearylthiodipropionate (DSTDP) → antioxidant
- Fatty alcohols
- Irganox MD1024 → antioxidant
- Free fatty acids
- Metallic salts of free fatty acids → antiacid
- Fatty amid (similar to erucamid) → lubricant
- Esters of glycerol (mono and di-esters similar to Atmer 122) → antistatic
- Ethoxylated fatty amid (similar to Armostat 2000) → antistatic
- Chimassorb 944 → UV stabilizer

◆ Quantitative extractions

□ **quantification by HPLC for**

**Irgafos 168
Irganox 1010
Irganox MD 1024
Tinuvin 326**

□ **quantification by GC for**

**fatty amid
DSTDP
esters of glycerol
ethoxylated fatty amid ***

*** Analysis by GC-MS to confirm the presence of ethoxylated fatty amid**

- ◆ **Quantitative determination for Chimassorb 944 (HALS)***
 - **treatment of the glassware to prevent the adsorption of HALS**
 - **fractionation**
 - **quantify densitometry by TLC**

*** method developed at the laboratory**

◆ Remarks

- the amount of DSTDP discloses a good agreement with the amount of S measured by X-ray Fluorescence
- the presence of Tinuvin 326 can partially explain the presence of Cl measured by X-ray Fluorescence
- the amount of Irgafos 168 is not in line correlation with the amount of P measured by X-ray Fluorescence

But we find free fatty alcohols and therefore we can suppose the presence of Weston 618 / 619 (alkyle phosphite) hydrolyzed.

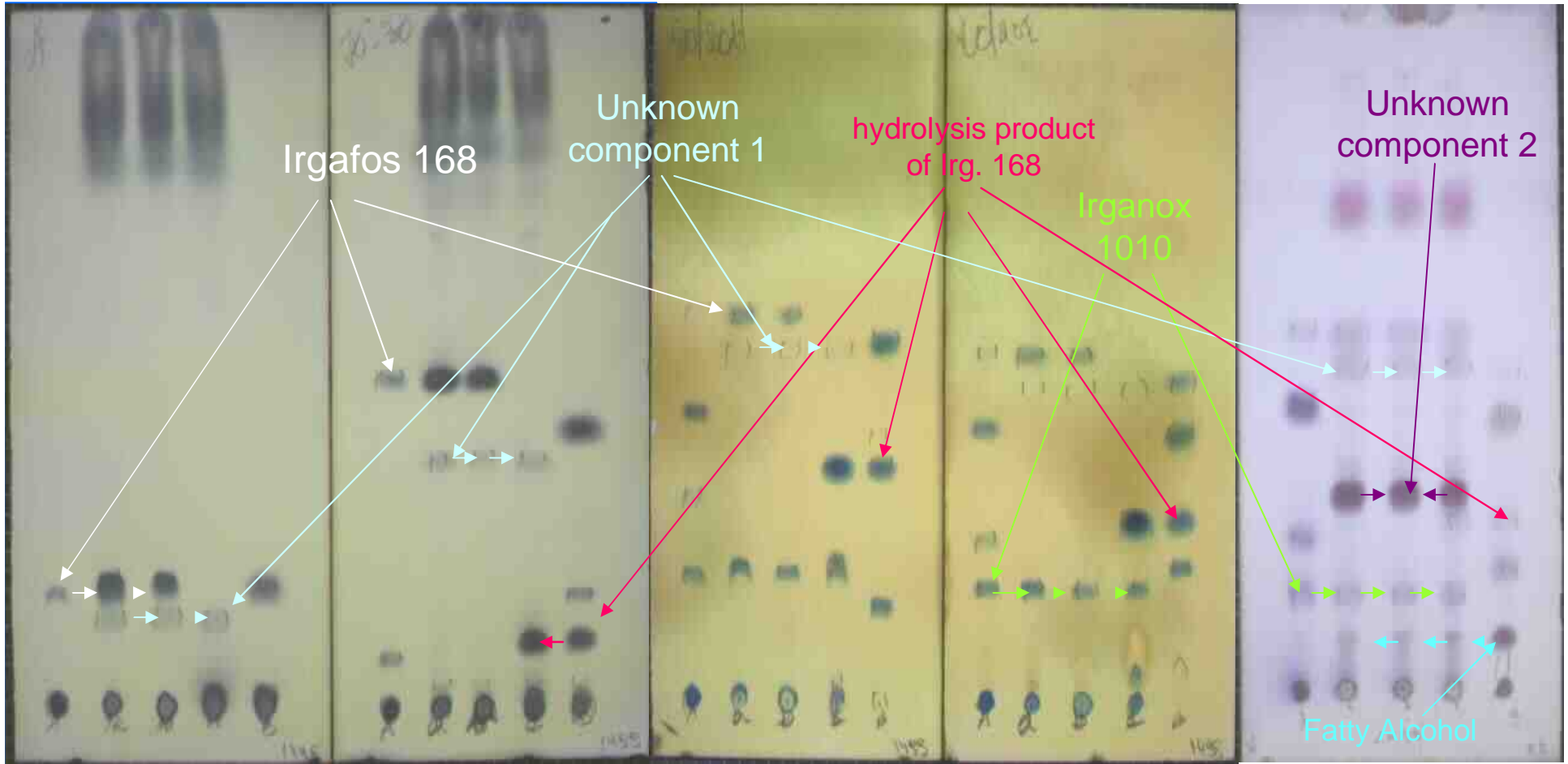


General conclusion

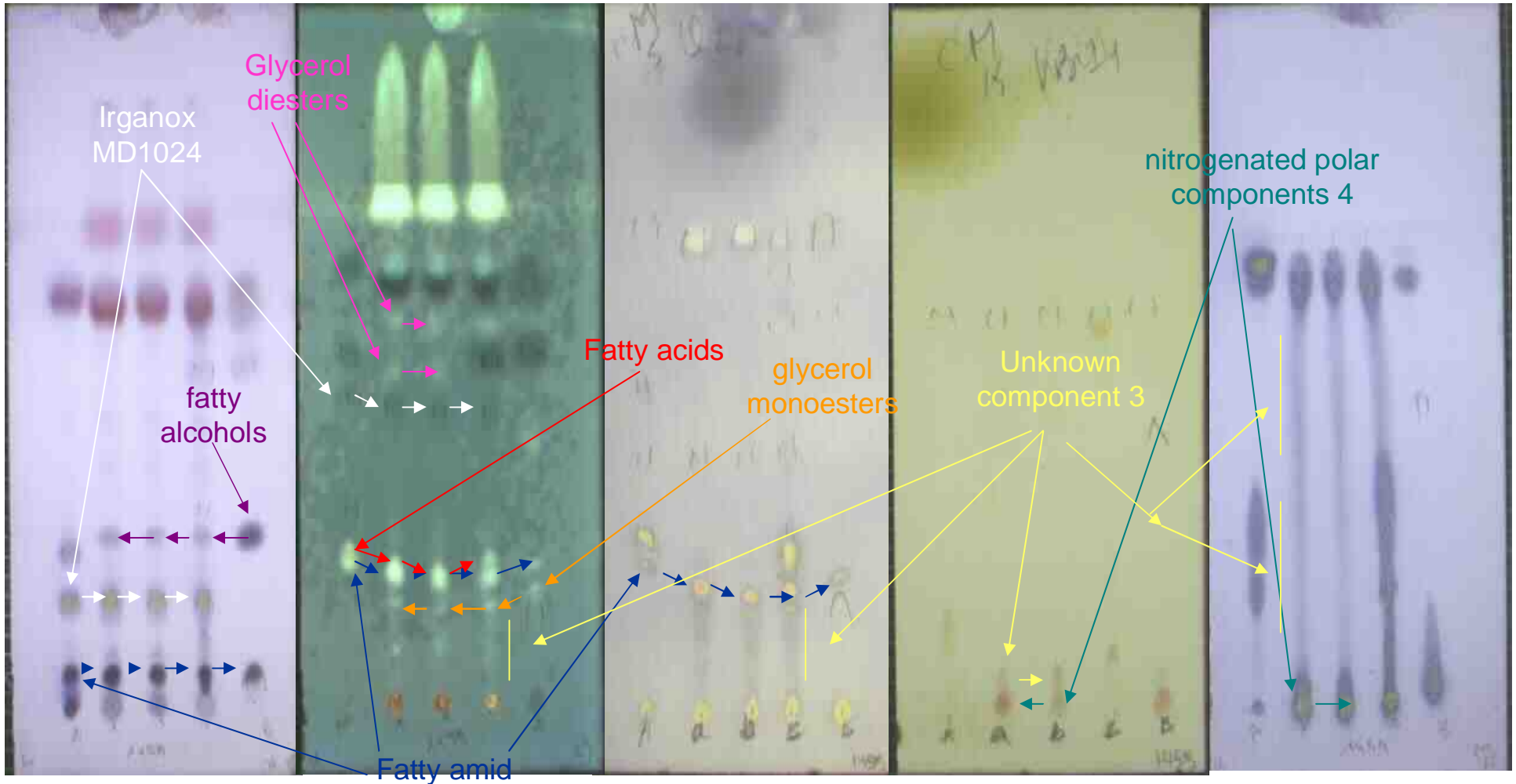
- ◆ **Using relevant fractionation procedures followed by adequate analytical techniques, polymers can be fully reformulated. This concerns :**
 - **all types of polymers**
 - **(also) polymer mixtures as well as multilayers**
 - **all types of additives and/or mixture of additives**

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General conclusion



General conclusion



General conclusion

