NATURAL POLYMERS
Polysaccharide I
STARCH 1

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Time schedule

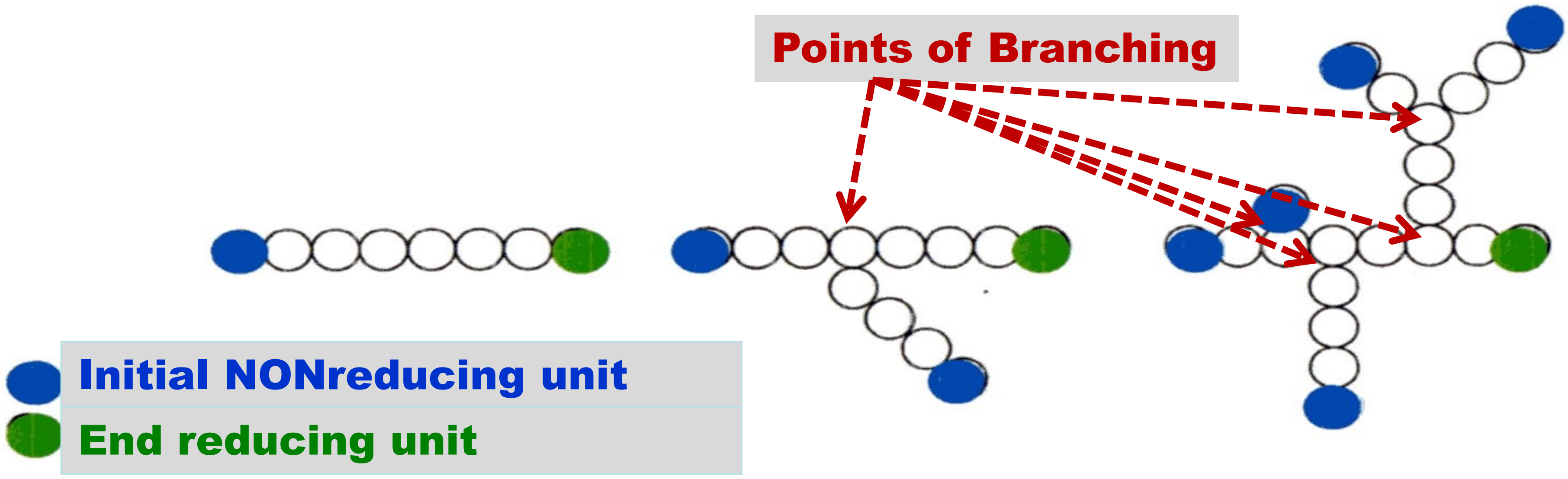
LECTURE	SUBJECT
1	Introduction to the subject – Structure & Terminology of nature polymers, literature
2	Derivatives of acids – natural resins, drying oils, shellac
3	Waxes
4	Plant (vegetable) gums, Polyterpene – natural rubber (extracting, processing and modification), Taraxacum_kok-saghyz
5	Polyphenol – lignin, humic acids
6	Polysaccharides I – starch
7	Polysaccharides II – cellulose
8	Protein fibres I
9	Protein fibres II
10	Casein, whey, protein of eggs
11	Identification of natural polymers
	Laboratory methods of natural polymers’ evaluation

POLYSACCHARIDES - DEFINITION

Polysaccharides are polymeric carbohydrate molecules composed of long chains of monosaccharide units bound together by glycosidic linkages, and on hydrolysis give the constituent monosaccharides or oligosaccharides. They range in structure from linear to highly branched. Polysaccharides are often quite heterogeneous, containing slight modifications of the repeating unit.

When all the monosaccharides in a polysaccharide are the same type, the polysaccharide is called a *homopolysaccharide* or *homoglycan*, but when more than one type of monosaccharide is present they are called *heteropolysaccharides* or *heteroglycans.*

When the repeating units in the polymer backbone are six-carbon monosaccharides, as is often the case, the general formula simplifies to $(C_6H_{10}O_5)_n$, where typically $40 \leq n \leq 3000$.



LITERATURE BOOKS

- **Thermoplastic Starch**
  - ISBN: 978-3-527-32528-3
- **Starches**
  - ISBN: 978-1-4200-8023-0
- **Starch – Chemisty and Technology**
  - ISBN: 978-0-12-746275-2

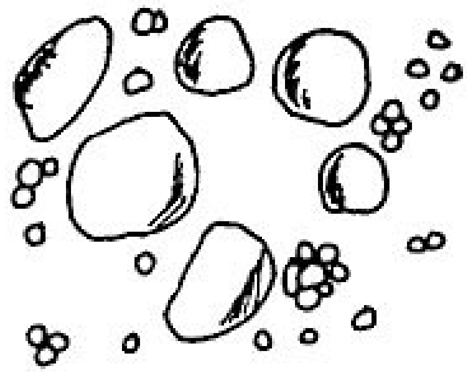
LITERATURE – JOURNALS

- **Starch - Stärke**
- **Journal of Carbohydrate Chemistry**
- **Carbohydrate Polymers *(Impact Factor: 5,1 !!!)***

1. **Sorts of Starch**
2. **Production of Starch**
3. **Starch Chemistry**
4. **Starch utilisation**
5. **Starch Modification**
6. **Production of Dextrin**
7. **Dextrin use**

Sorts of the Industry important Starches

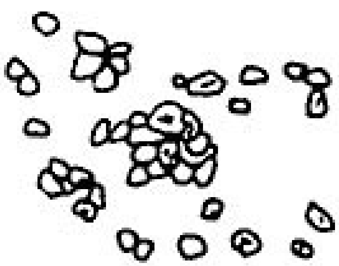
a



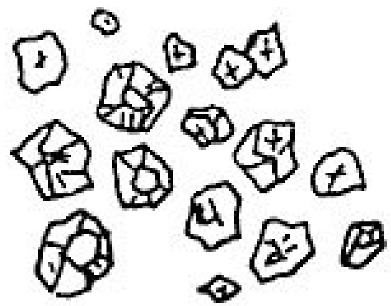
b

Two Sorts of Grains!

Grain (Particles) shapes



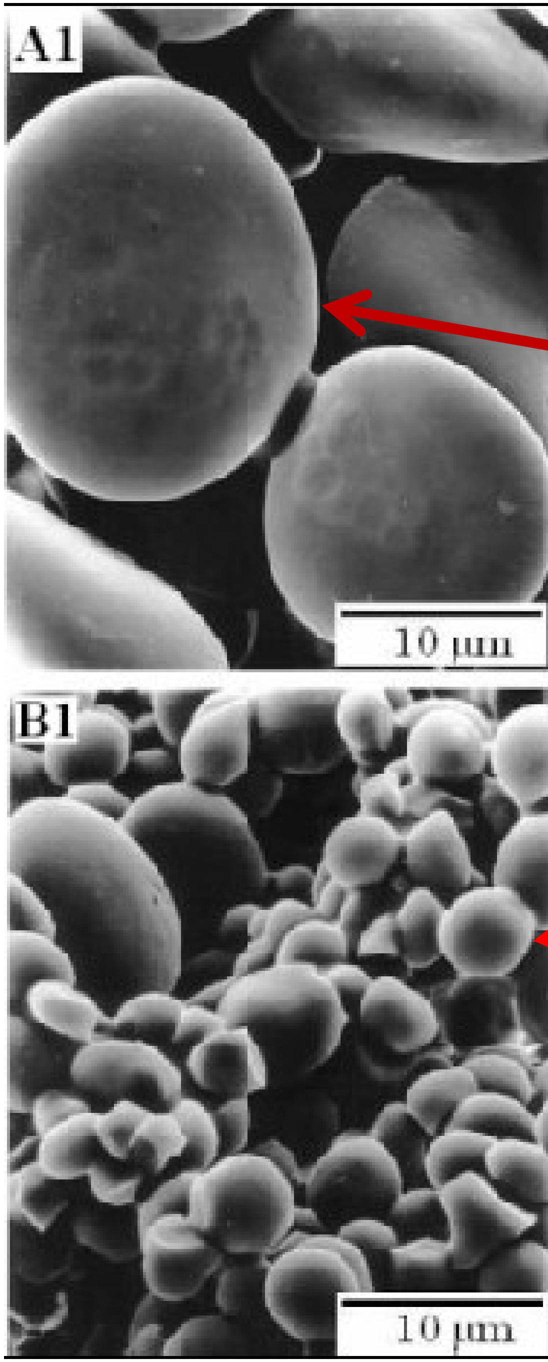
c

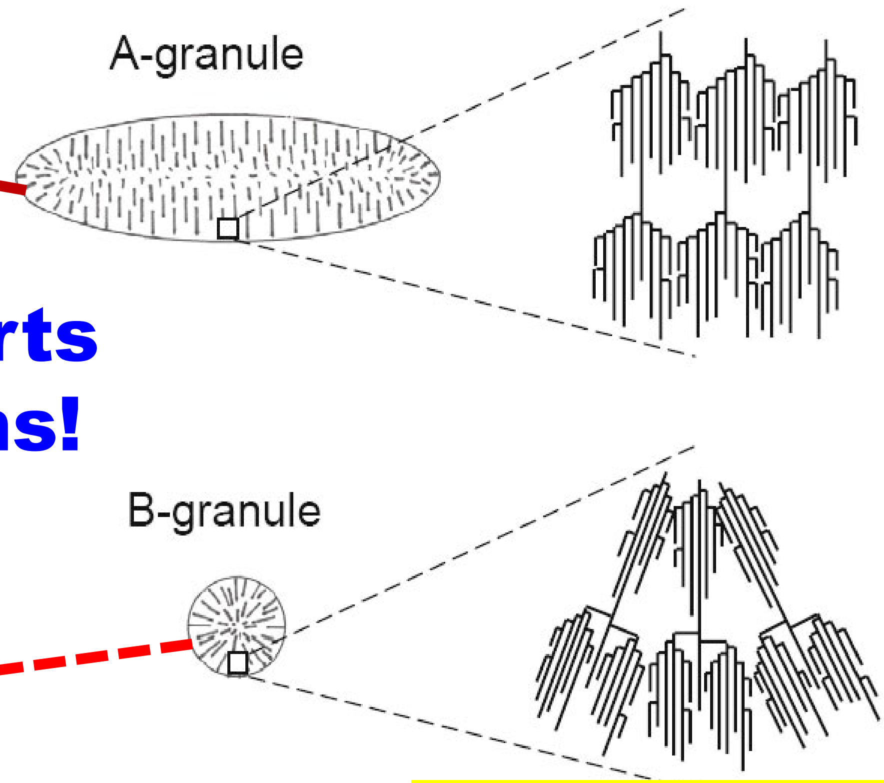


d

The Characteristic shape of the STARCH GRAINS a) Potato, b) Wheat, c) Rice, d) Corn

WHEAT STARCH



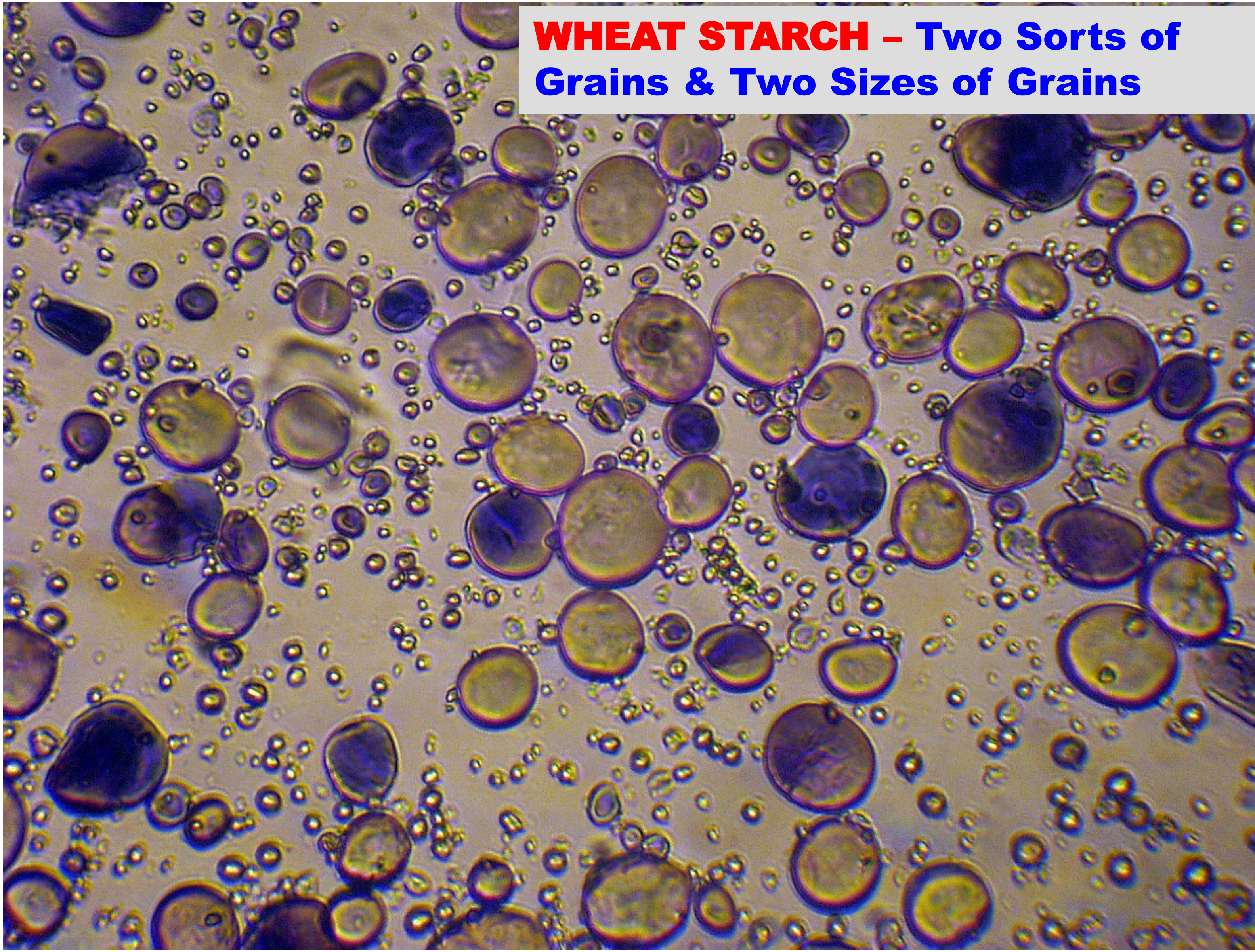


Two Sorts of Grains!

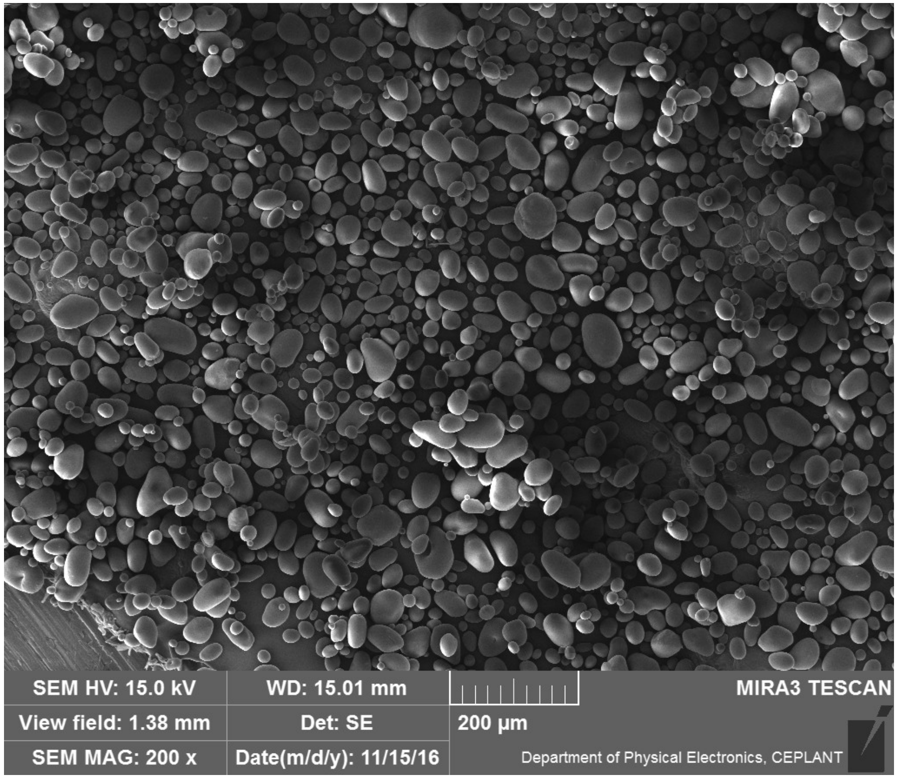
Two Grain shapes

The Different Branching

WHEAT STARCH – Two Sorts of Grains & Two Sizes of Grains

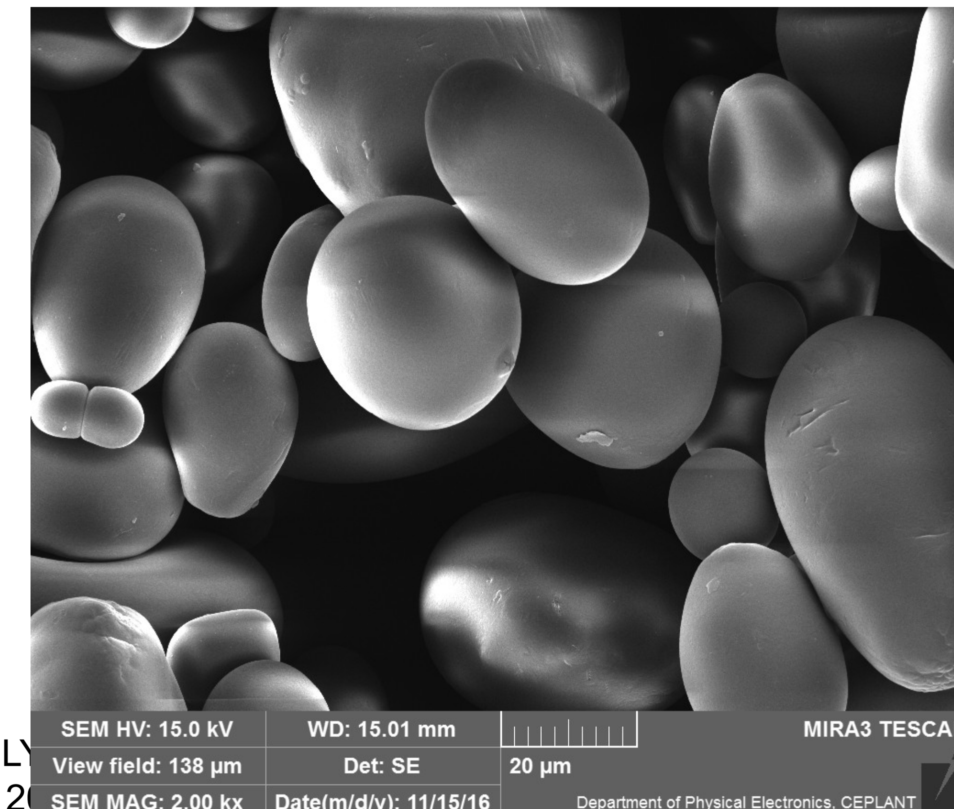


Starch SEM – my own Work at MU 1

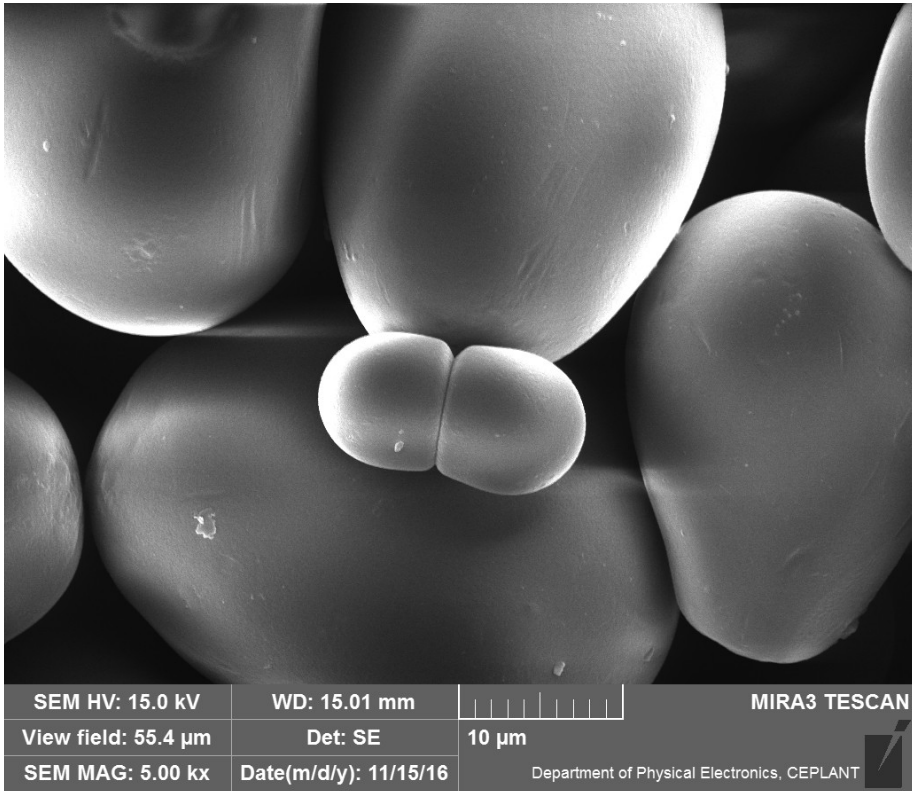


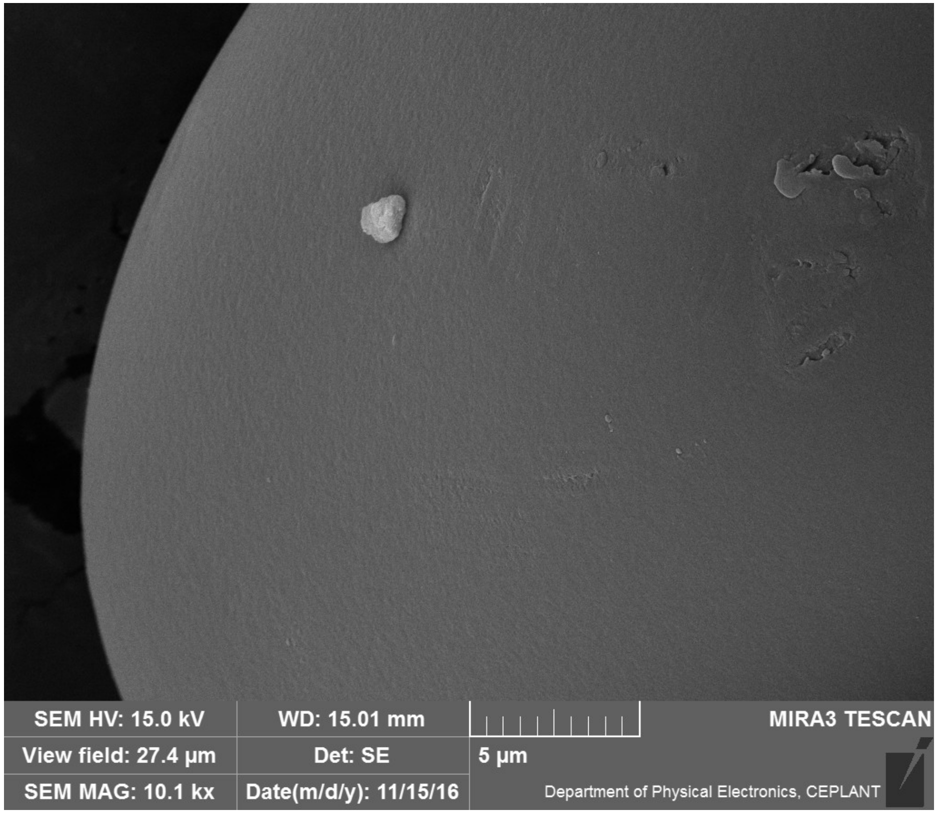
You didn't see any Surface Wrinkling, as you can see on the Pictures drawn and taken from a Literature.
The Reason IS PROBABLY IN THAT, because the Starch grains were not dried before taking the SEM Pictures.

Potato Starch



Starch SEM – my own Work at MU 2

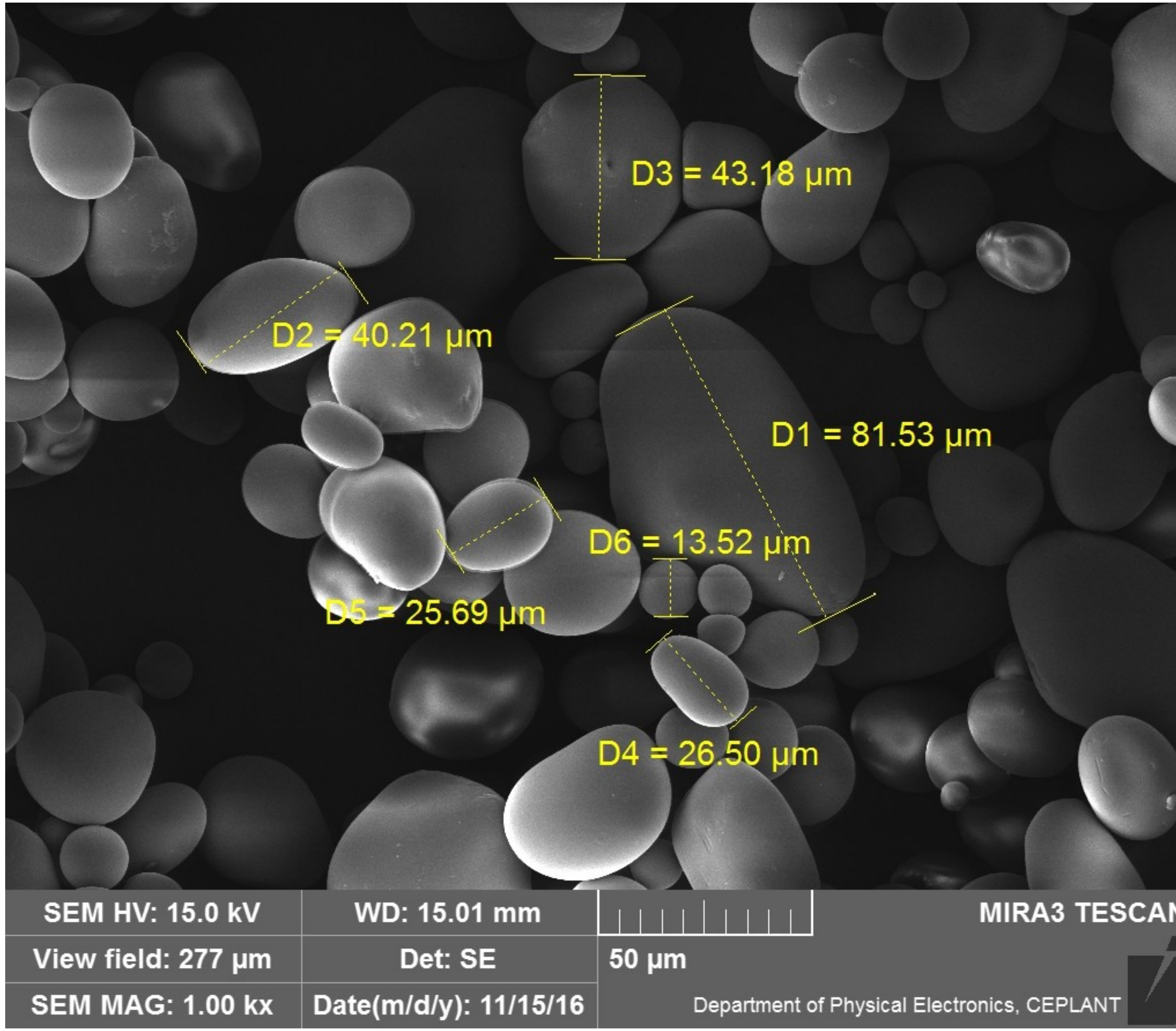




Potato Starch

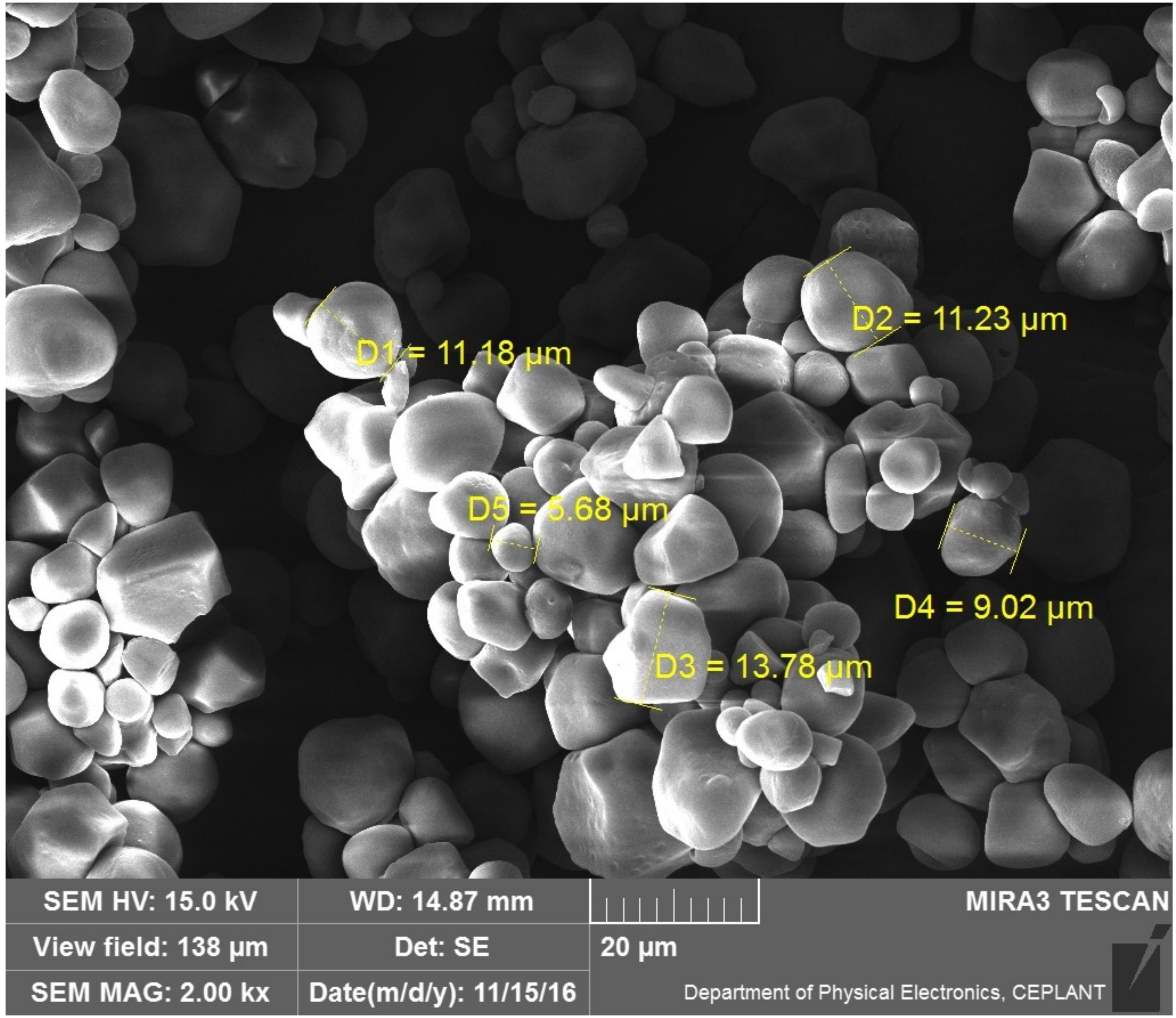
Starch SEM – my own Work at MU 3

Potato Starch



Starch SEM – my own Work at MU 4

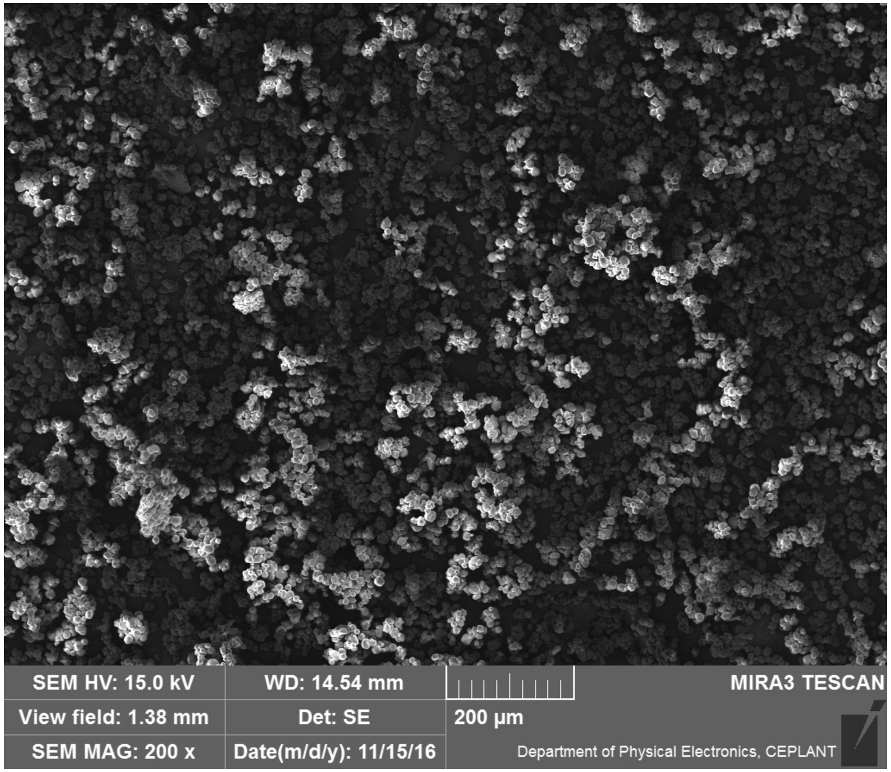
Corn (Maize) Starch



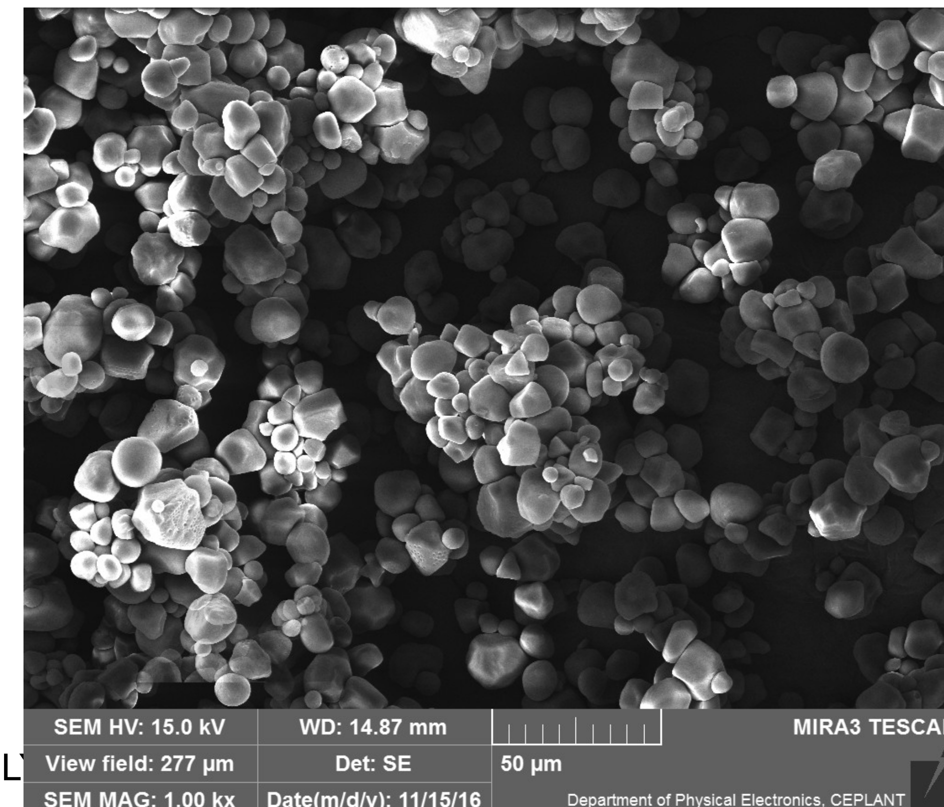
Starch SEM – my own Work at MU 5

You didn't see any Surface Wrinkling, as you can see on the Pictures drawn and taken from a Literature.

The Reason IS PROBABLY IN THAT, because the Starch grains were not dried before taking the SEM Pictures.

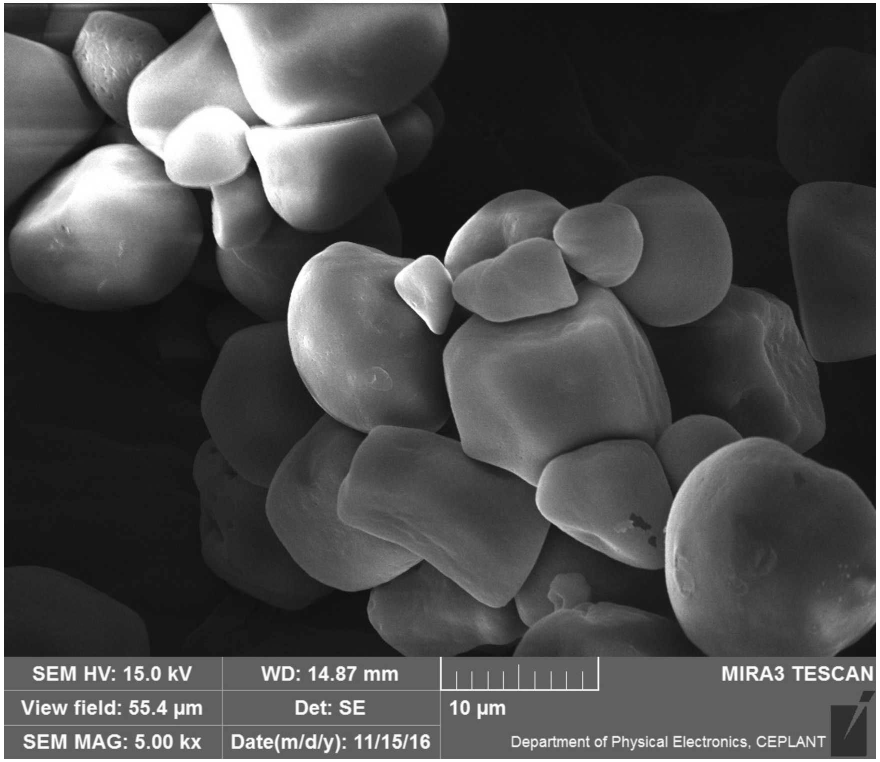


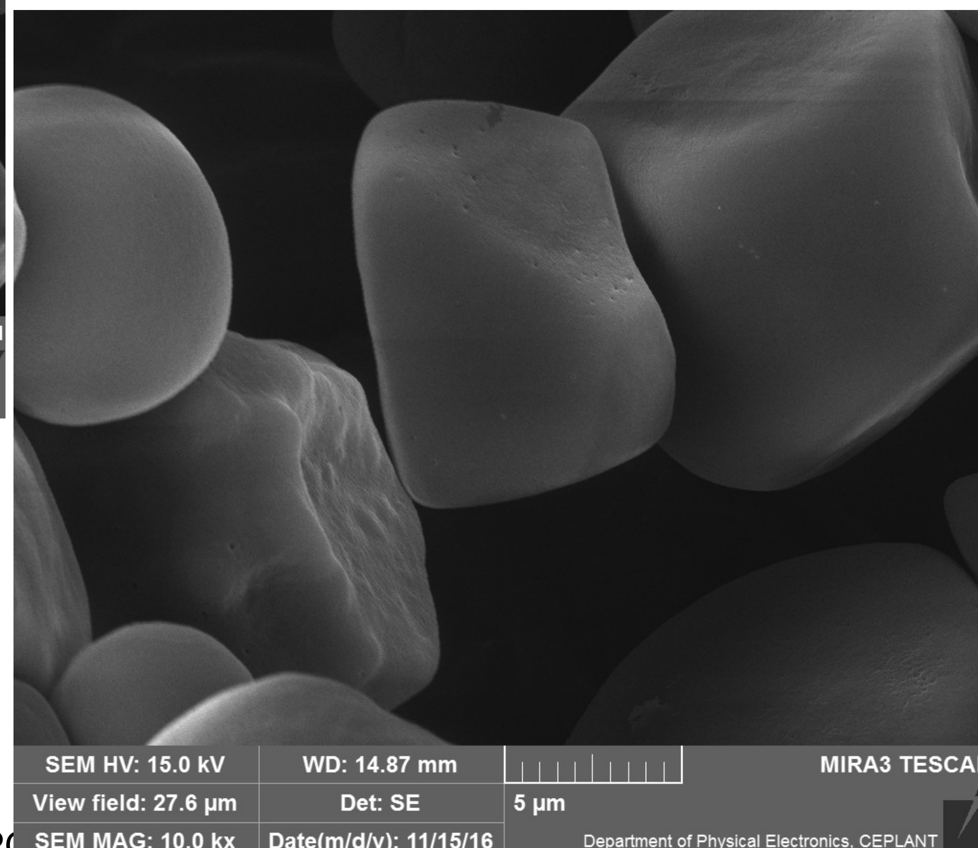
Corn (Maize) Starch



Starch SEM – my own Work at MU 6

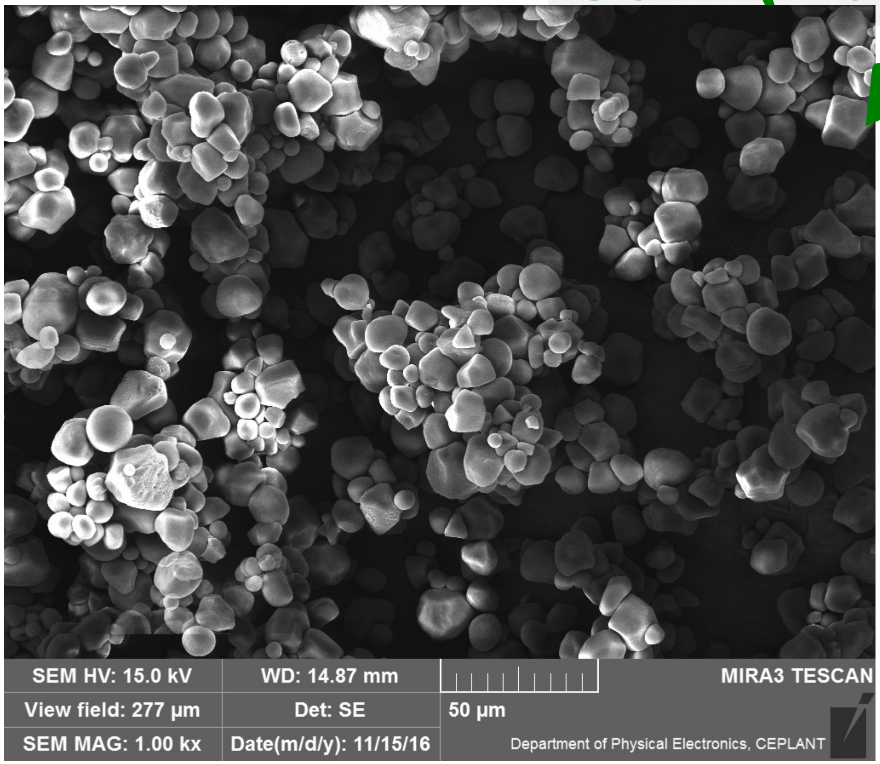
Corn (Maize) Starch

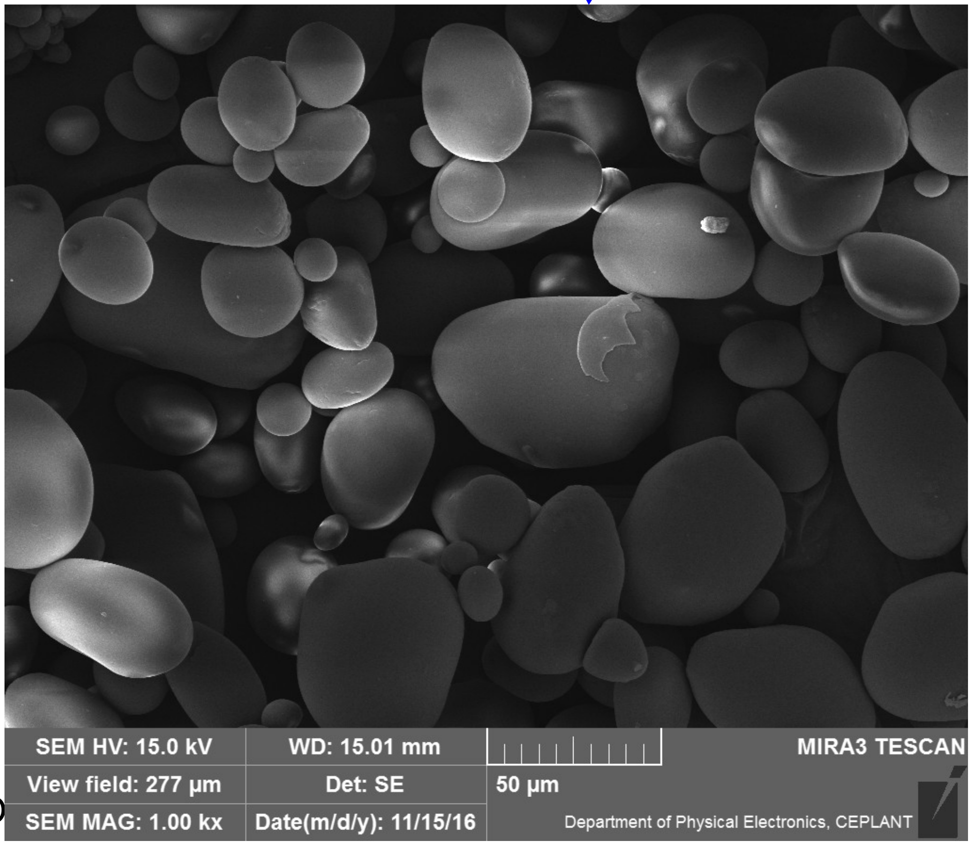




Starch SEM –my own Work at MU 7

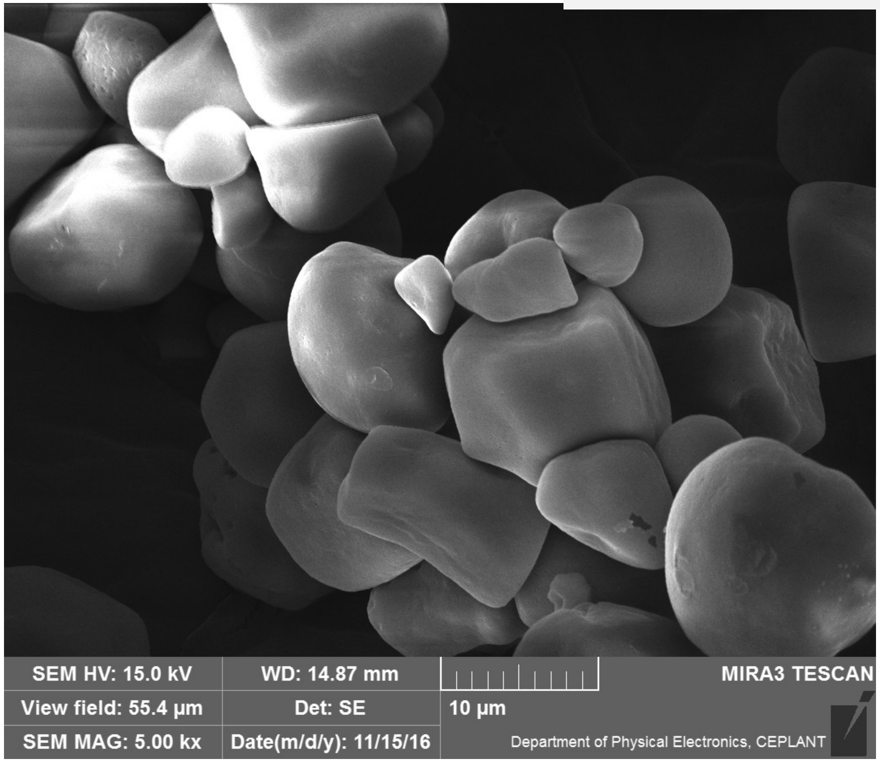
Corn (Maize) Starch X Potato Starch

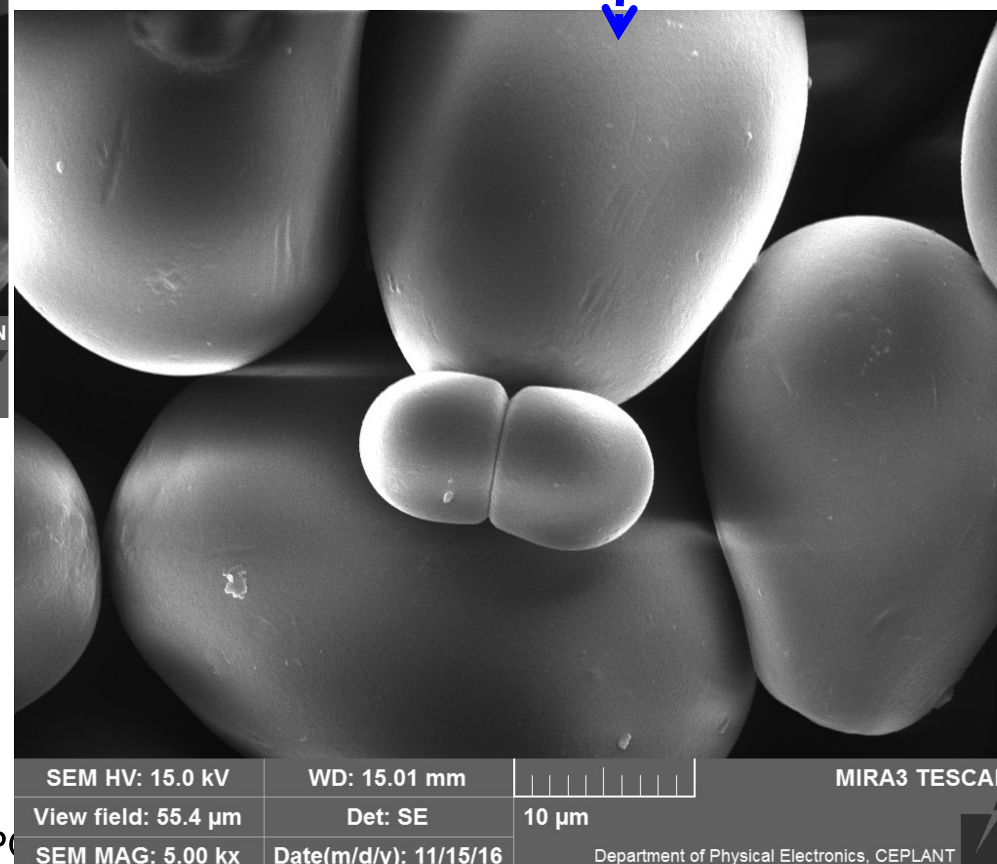




Starch SEM –my own Work at MU 8

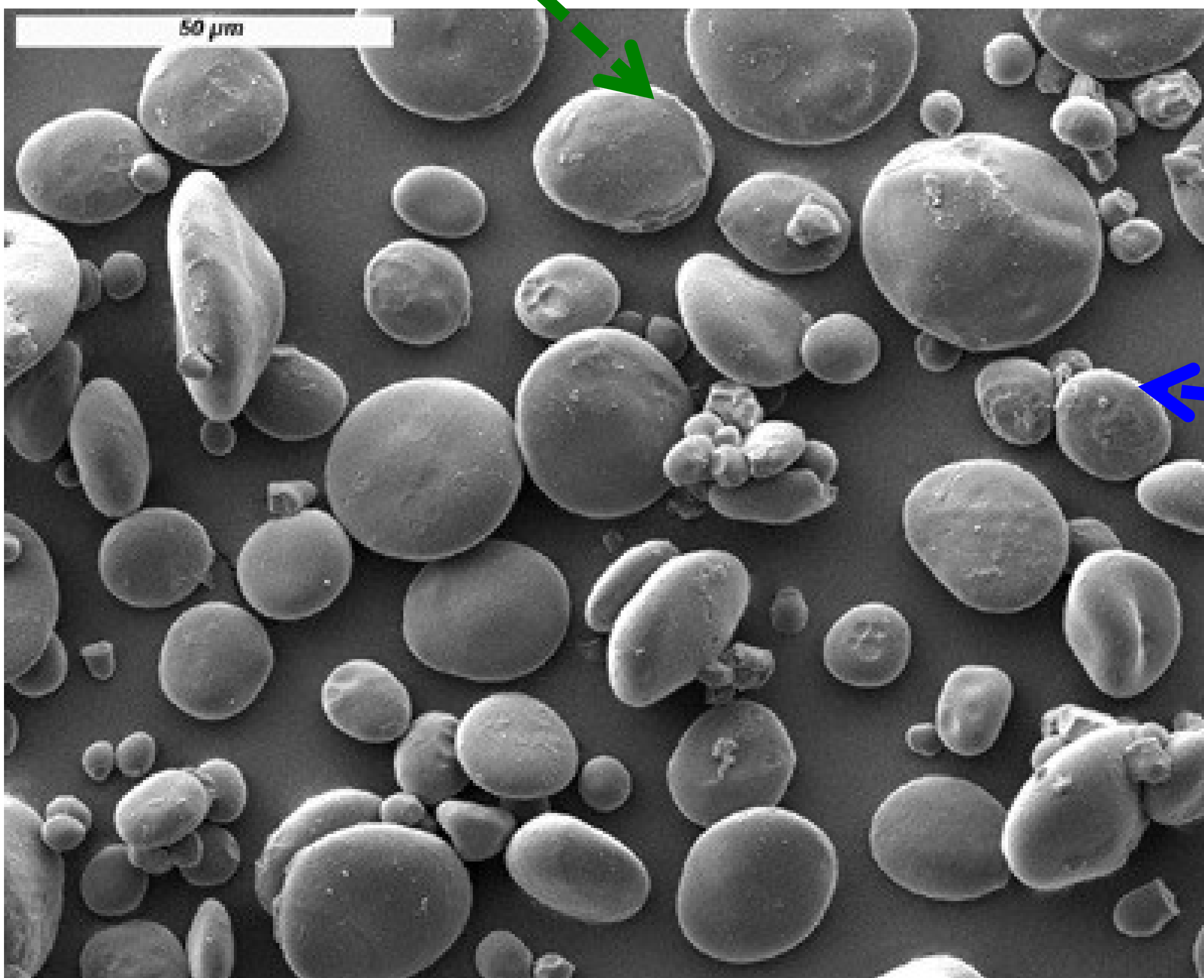
Corn (Maize) Starch X Potato Starch





Starch SEM – WHEAT
(taken form Literature)

A-Grain



B Grain

Sizes of Starch Grains (Particles)

- **Potato** : predominantly 10 – 70 μm (BROAD Grains' sizes distribution)
- **Corn**: predominantly 20 μm (NARROW Grains' sizes distribution)
- **Wheat**: Two Sorts of Grains
  - Size 1 – 10 μm > **Starch B** (Waste product, **contains Proteins**)
  - ***Size 10 – 25 μm > Starch B (PRODUCT)***
- **Rice**: predominantly approx. 5 μm (NARROW Grains' sizes distribution)

STARCH - Production and Use *(Data from the Years 1991 & 2011)*

- World Production (1991): 22 000 000 tons
- **World Production (2011): 70 000 000 tons**
- **Corn STARCH** : **15 000 000 tons**
- **The most important plants utilized to STARCH production:** CORN, Potato, Rise, Cassava
- **The principal STARCH Producers:** USA (**CORN**), former USSR republics, Netherland, Germany, Poland (**Potato**)
- **Nutrition use:** approx. 70 %
- **Modified STARCH :approx.** 5 000 000 tons

World Production of the SYNTHETIC PLASTICS is approx 300 000 000 t/annual

Cassava

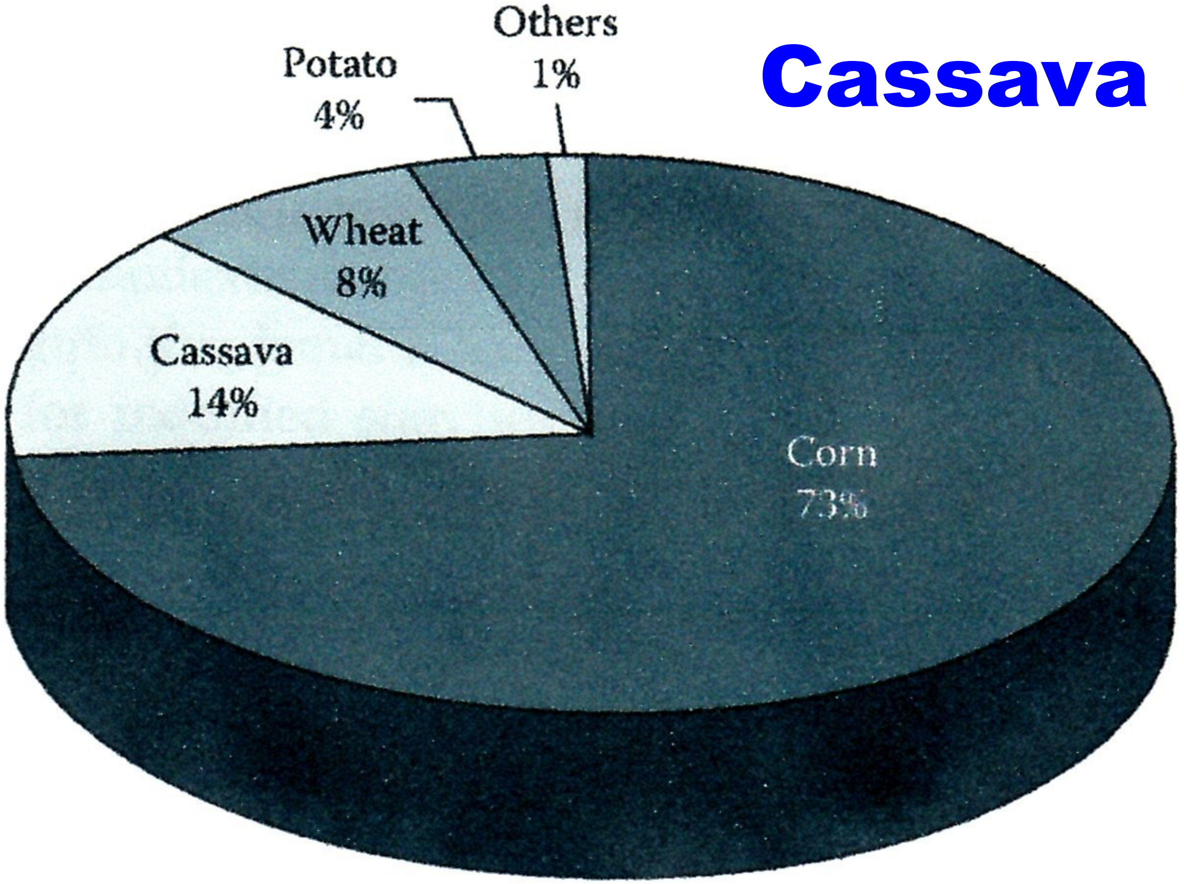


Figure 1.3 Starch production according to botanic sources. Source: Röper and Elvers (2008).

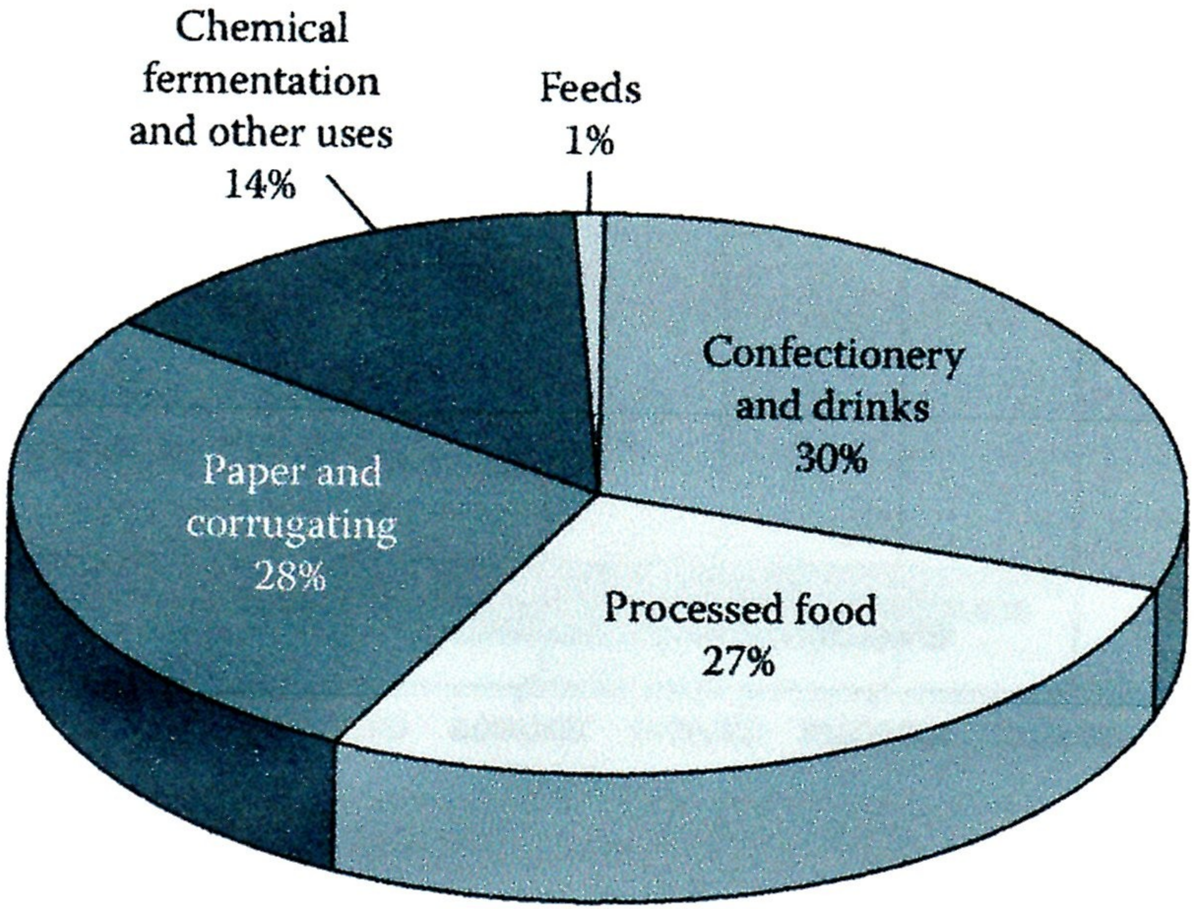


Figure 1.5 Use of starches and their derivatives by European industries. Source: Röper and Elvers (2008).

World Production of the SYNTHETIC PLASTICS is approx 300 000 000 t/annual

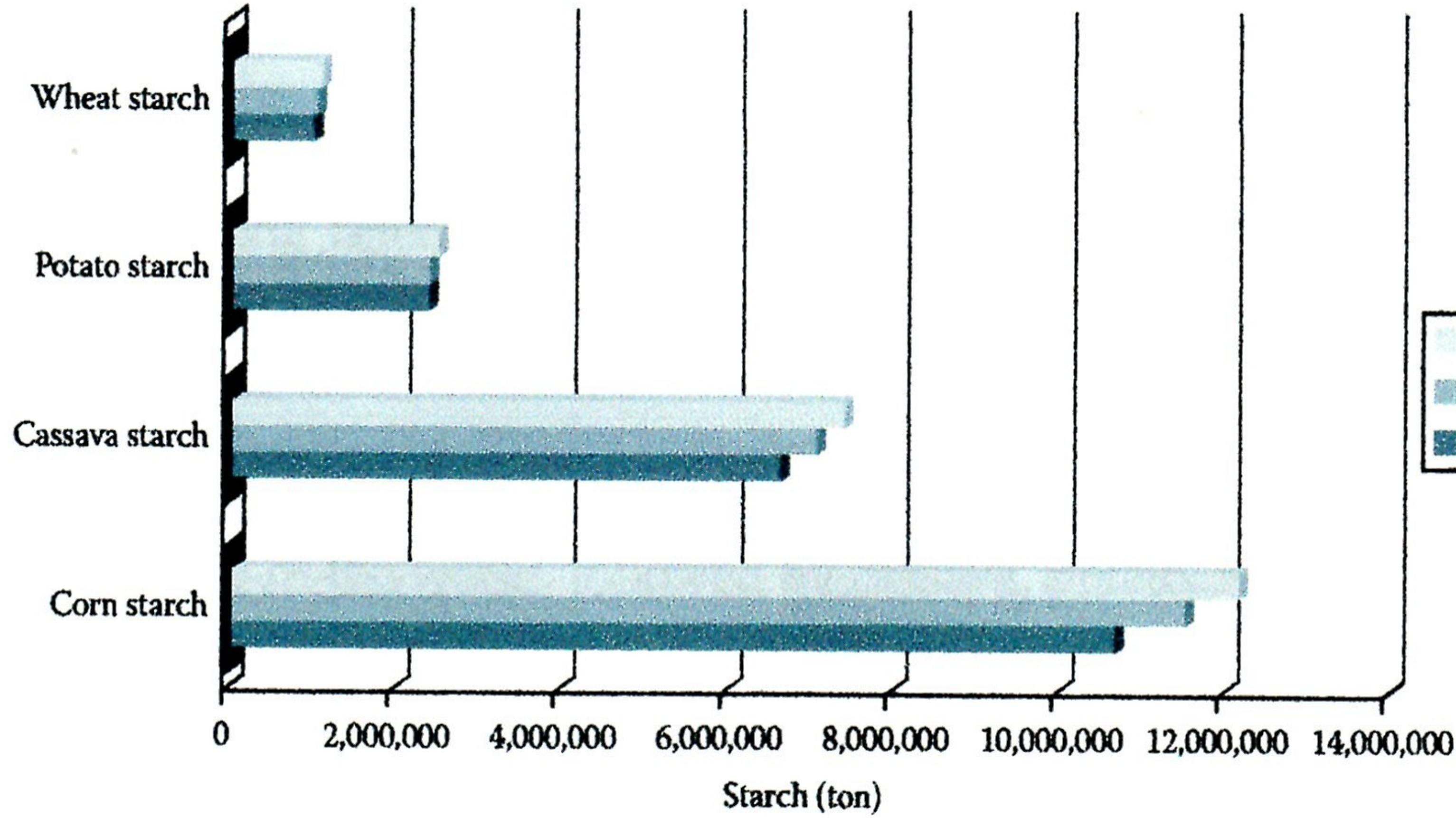


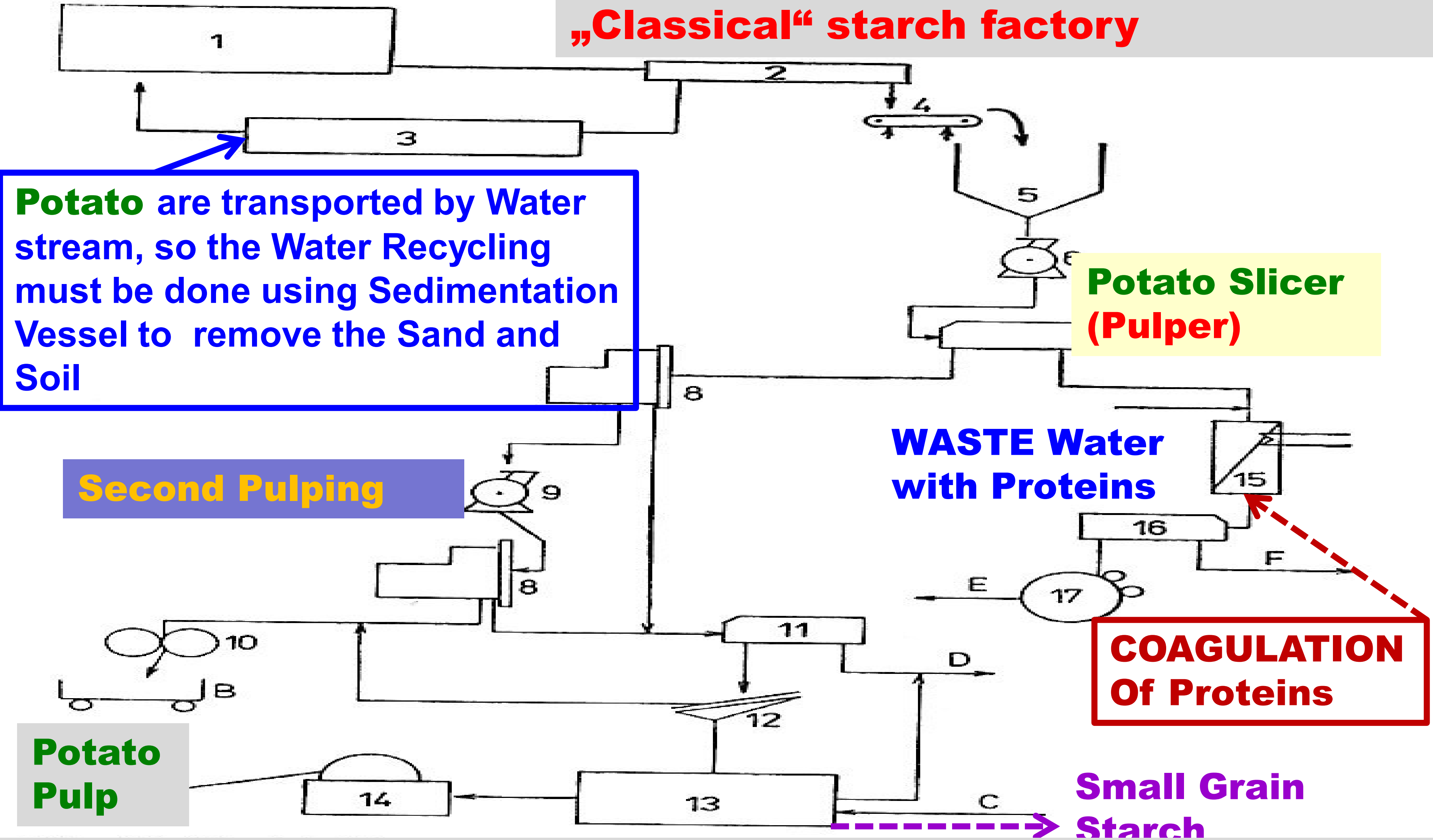
Figure 1.4 Amounts of starches used as food ingredients, dextrins, paper coatings, and adhesives between 2005 and 2007. Source: LCM (2008).

STARCH - Production from Potato 1

- **Potato** contain 14 – 21 % w/w of Starch, which is not so much
- It is possible to take approx. 4 tons of Starch from 1 ha of the Cultivated field
- The Water Need is for the production, up to 3,5 – 8 m^3/ton of Potato, but more modern Technologies can lower this Volume

P_2O_5	0,176 %	K_2O	0,018 %
SiO_2	0,069 %	Na_2O	0,008 %
SO_3	0,008 %	Fe_2O_3	stopy
CaO	0,059 %	Nitrogen compounds	0,011 %
Mg	0,001 %	Lipids	0,040 %

„Classical“ starch factory



1. Potato Depot, 2. Washing machine, 3. Sedimentation Vessel, 4. Belt scales, 5. Potato hopper, 6. Potato slicer, 7. Centrifuge, 8. Wash out (Starch) machine, 9. Second Pulping, 10. Potato pulp Press, 11. Centrifuge, 12. Mesh, 13. Starch size sorting (Starch refining), 14. Filter, 15. Preheating, 16. Centrifuge, 17. Roller dryer

A – Starch, B - Potato pulp, C – Clean Water, D – Waste Water, E – Dry protein, F – Liquid animal feed

FROM THE STARCH TO ETHANOL

- **STARCH**
  - **ENZYME from the Grain malt**
    - **Monosaccharide**
      - **ENZYME from the Yeast**
        - » **ETHANOL**

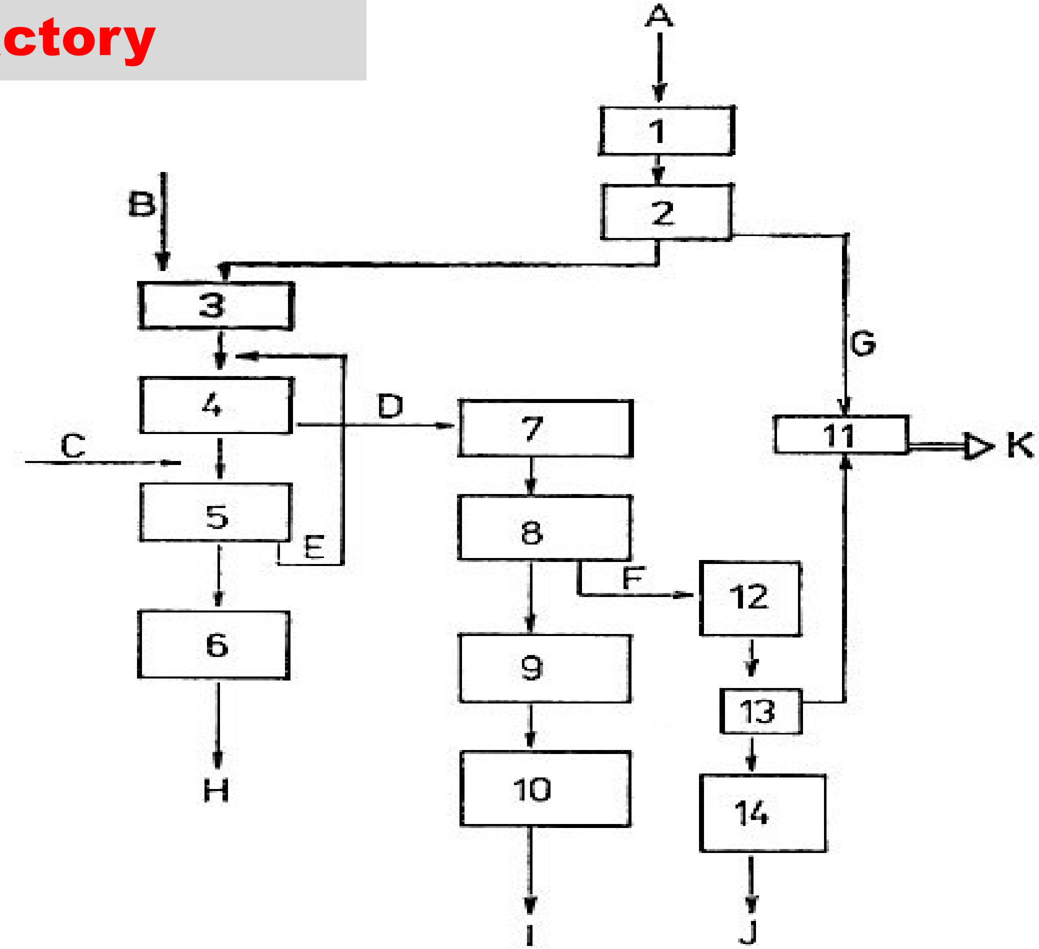
STARCH - Production from Potato 2

- **Starch factory is usually combined with Agricultural alcohol Distillery**
- **Raw Materials for this Distillery:**
  - **Fine Fraction of Starch gained during so called STARCH SIZE SORTING (STARCH REFINING),**
  - **WASTE Water with Proteins gained during Centrifuging of the Starch Pulp**
  - **Potato pulp after Washing out the Starch by Water (It can be used as the Animal feed also)**

STARCH - Production from Wheat

- **Wheat** flour contains approx. 68 % w/w of Starch, what is really much,
- It is possible to take approx. 4 tons of Starch from 1 ha of the Cultivated field, so it is the same Quantity as for Potato,
- The Water Need is for the production, approx. 3,5 m^3/ton of **Wheat** flour,
- It is possible to utilize the Fraction B also and the Waste protein (Gluten)
- Dry matter of this Starch is approx. 84 % w/w

Wheat starch factory



Nothing goes to Waste here!

Small Grains B Starch are separated and are processed in the Separate Branches I and J

1. Mill, 2. Washing machine, 3. Flour sifting machine, 4. Separator, 5. Separator, 6. Evaporator, 7. Mixer, 8. Water suction device, 9. Dryer, 10. Mill, 11. Animal feed Mixer, 12. Reactor for Hydrolysis, 13. Proteins Coagulation, 14. Evaporator

A – Wheat, B - Water, C – Water, D – Flour, E – Water returning Stream, F – Starch, G - Wheat middlings, H – Starch, I – Gluten, J – Protein, K - Animal feed

STARCH - Production from Corn

- Corn Grain for the Starch production has the following Composition:

Water	18,50 %	Fibre	2,40 %
Starch	55,50 %	Ash	1,50 %
Proteins	8,20 %	Pentosans	5,10 %
Oil	3,00 %	Other	5,80 %

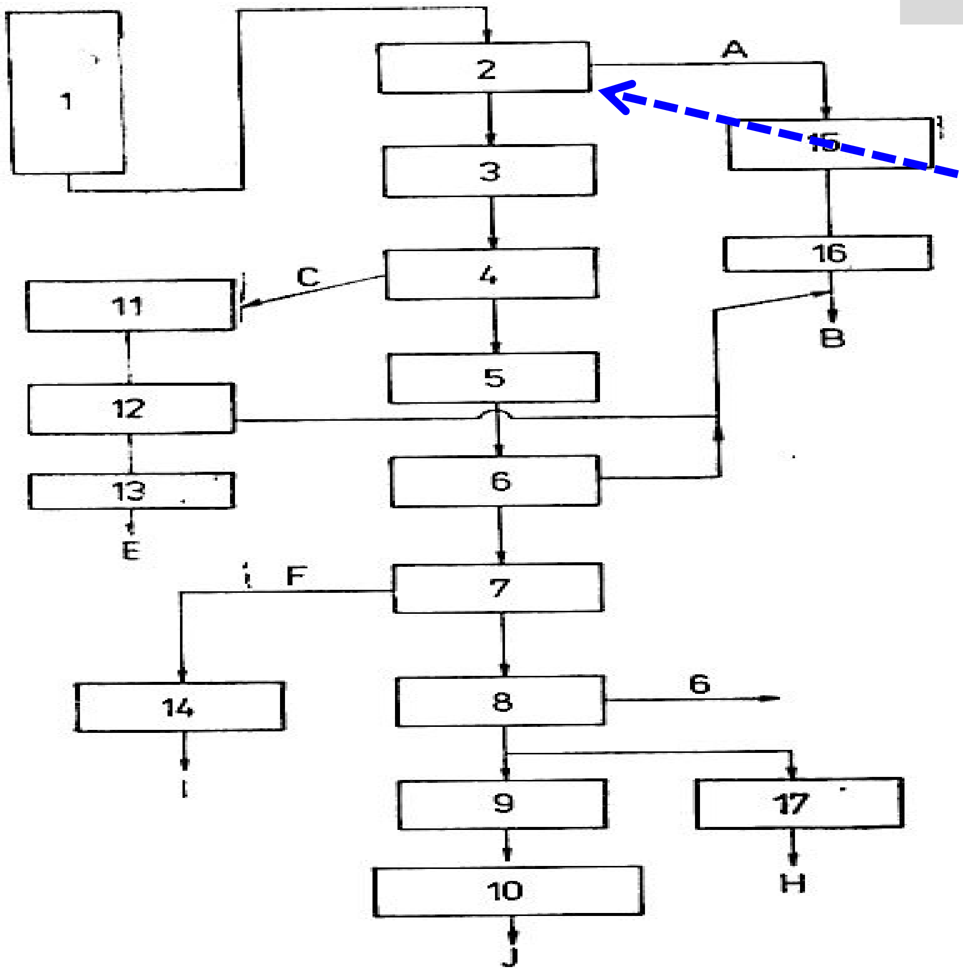
The Varieties has been cultivated, containing either mostly AMYLOSE or mostly AMYLOPECTIN

The Top Varieties having in the Grain up to 90 % w/w of Starch

The Water Need is for the production (m^3/ton of Corn) – **I do not know**

Dry matter of this Starch is approx. 84 % w/w

Corn starch factory



Very similar to Wheat starch factory, up to SOAKING

Nothing goes to Waste here!

1. Corn grain silo, 2. Soaking tank, 3. Sprout removing & Milling machine, 4. Sprout processing block, 5. Fine milling, 6. Fibre separation, 7. Liquid part separation, 8. Starch size sorting (Starch refining), 9. Filtration & Dryer, 10. Starch silo, 11. Sprout washing & Dryer, 12. Oil extraction, 13. Oil refining, 14.&15. Evaporator, 16. Drying, 17. Hopper

A – Soaking Water, B - Animal feed, C – Sprout, D – Fibre, E – Corn oil, F –Gluten Water, G - Waste Water, H – Starch Suspension for Modification or Syrup, I – Corn eluate (infusion), J – Starch

Starch Products for Food Industry

- **Sweets, Jam and Marmalade, Drinks, Bakery products, Pastry etc.**
- **Milk Products, Meat Products, Soup (especially dehydrated), Sauce, Salad dressing etc.**
- **Ice cream, Children's nutrition …**

Starch Products for NONFood Industry

Paper Industry

- SIZING IN THE MASS (MATTER),
- SURFACE SIZING,
- PASTING & PAINTING

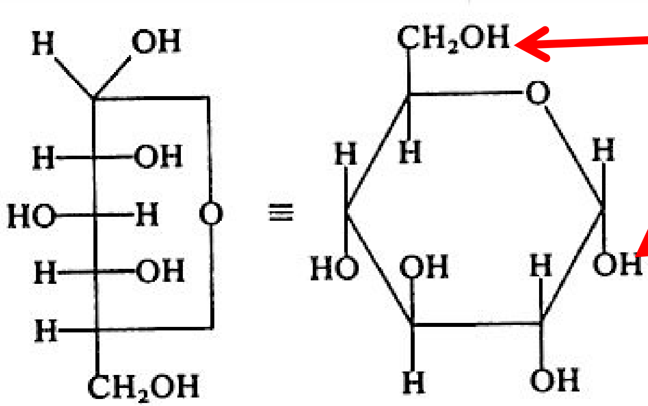
TEXTILE Industry

- Slashing, Printing, Final treatment, …..

Gluing

- Paperboard, Corrugated paperboard, Multilayer bags, Lamination, ………….

STARCH versus CELULLOSE 1

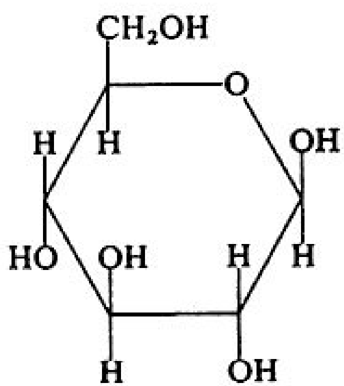


α-D-glukopyranosa
(α-glukosa)

They differ in the Position of $-CH_2OH$ toward to -OH

STARCH is the α-D-glukopyranose polymer

Dextrose

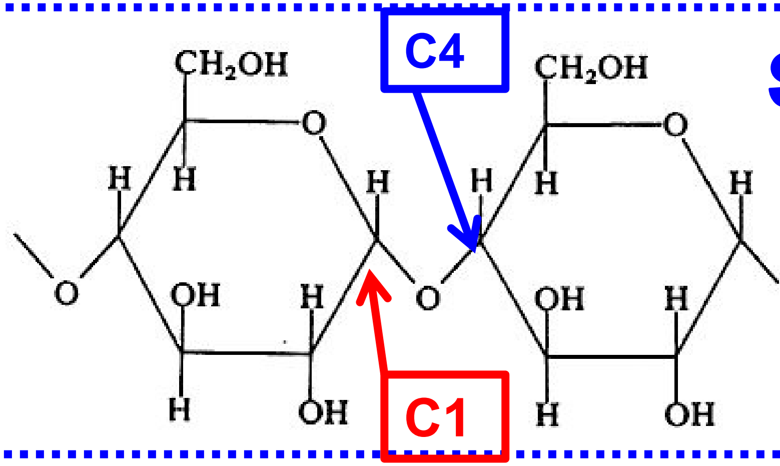


β-D-glukopyranosa
(β-glukosa)

CELULLOSE is the β-D-glukopyranose polymer

STARCH versus CELULLOSE 2

STARCH

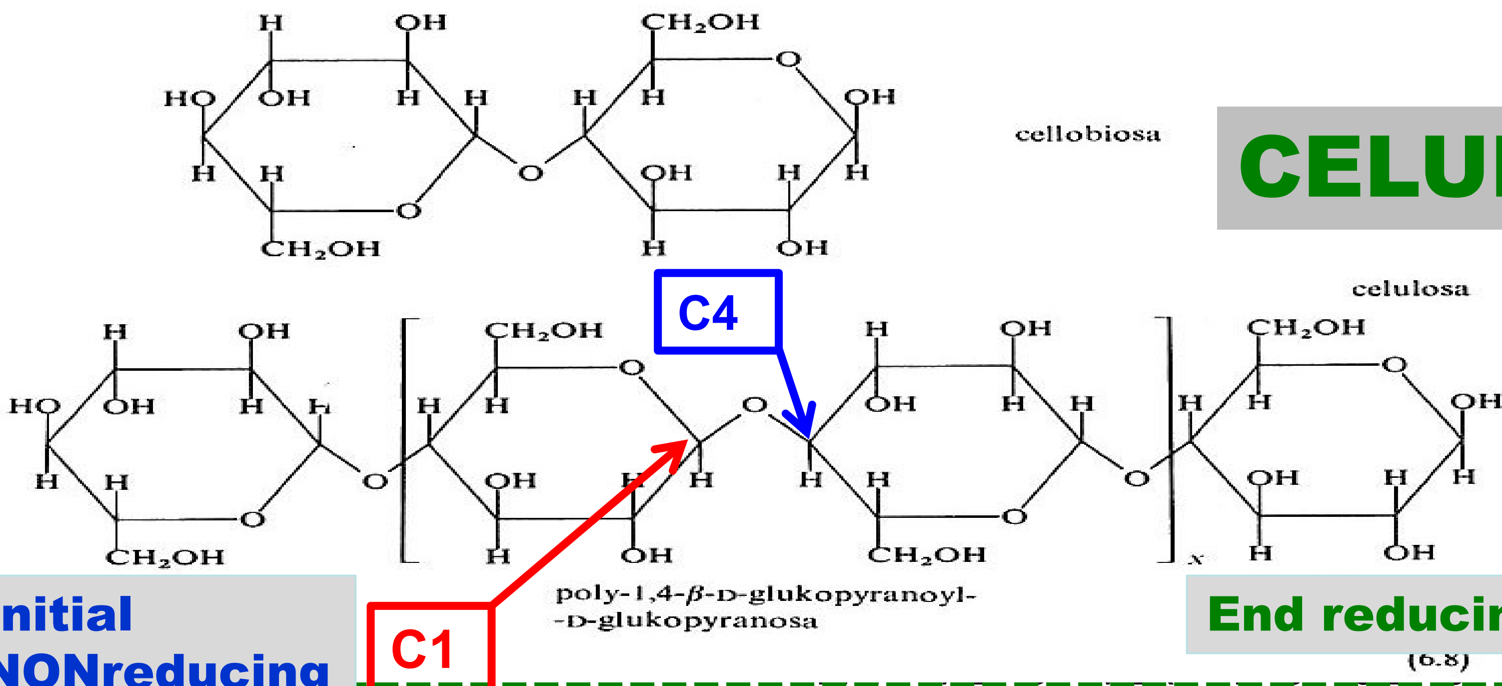


poly(1→4)-α-D-gluko-
pyranosa (amylosa)

Notice the Position of the Bond via Oxygen between the Glucose Units

CELULLOSE

cellobiosa



celulosa

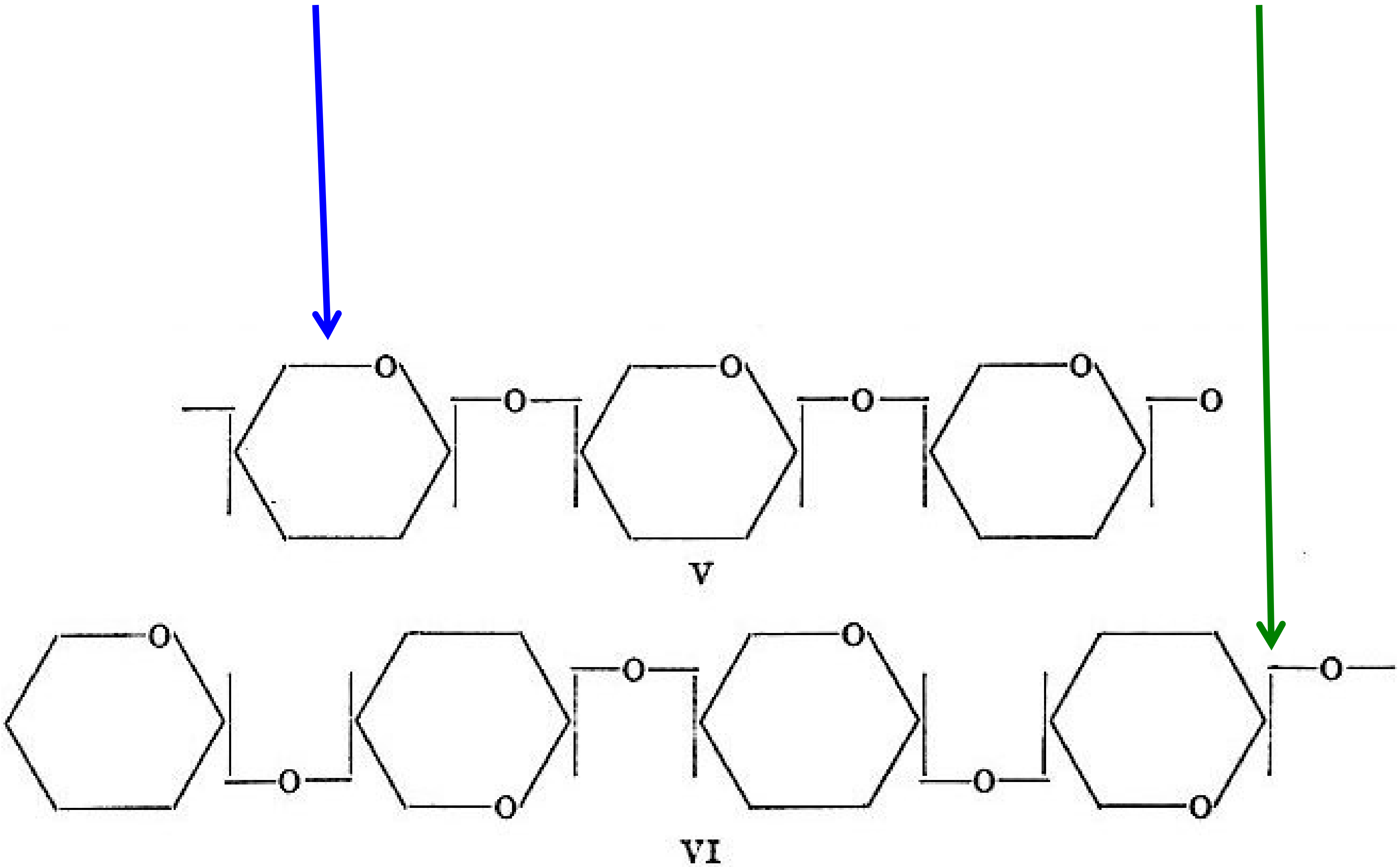
poly-1,4-β-D-glukopyranoyl-
-D-glukopyranosa

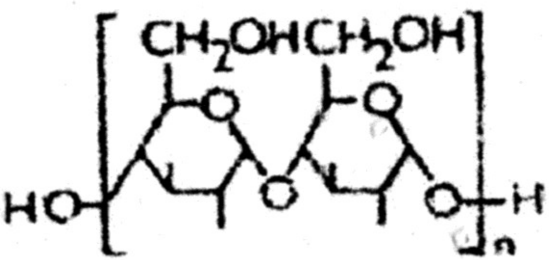
(6.8)

Initial NONreducing unit

End reducing unit

STARCH (amylose - linear) versus CELULLOSE 3





STARCH

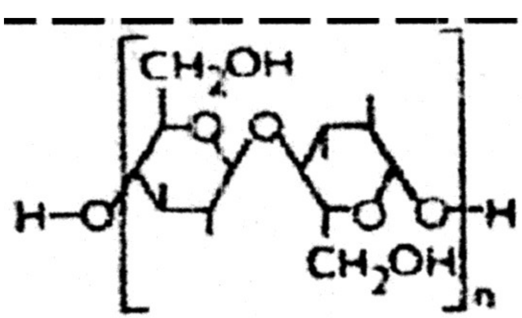
STARCH versus CELULLOSE 4

n = 1 > (1→4)–α–D-glukopyranosyl 1-α–D-glukopyranose ⇒ **MALTOSE**

n = 150 ..... 500 AMYLOSE

n = 550 ..... 7500 AMYLOPECTIN, Branching (1→6) on the approx. Each 8 to 10 GLUCOSE unit

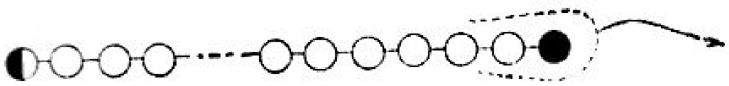
n = 1 > (1→4)–β–D-glukopyranosyl 1–β–D-glukopyranose ⇒**CELOBIOSE**

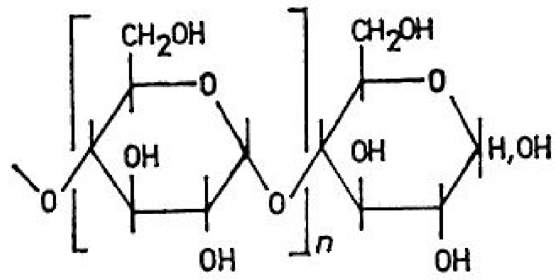


n = 1000 ..... 7000 CELULLOSE

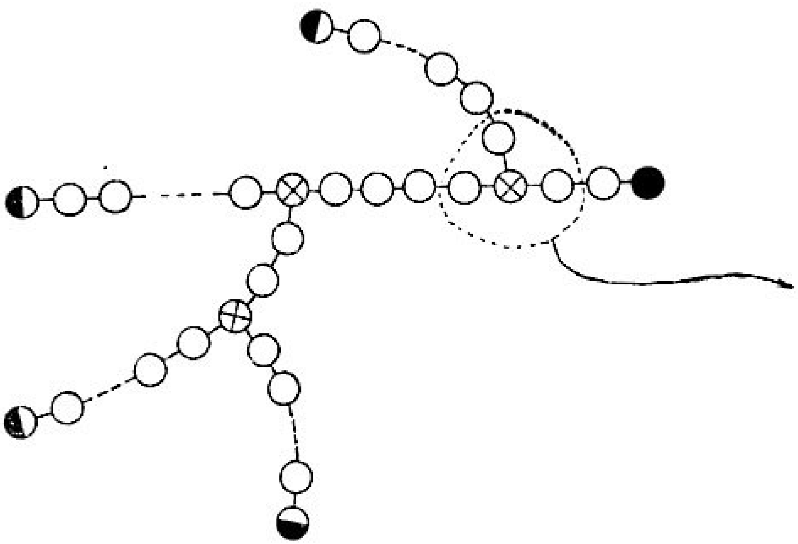
CELULLOSE

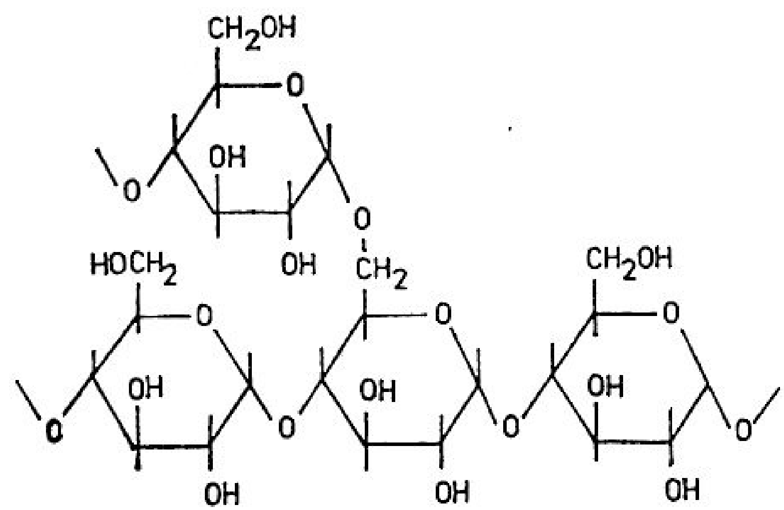
AMYLOSE & AMYLOPECTIN 1





AMYLOSE

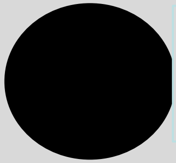




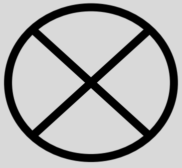
AMYLOPECTIN

AMYLOSE (Picture up)

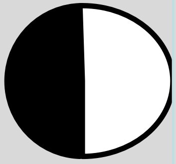
AMYLOPECTIN (Picture down)



End reducing unit



Point of Branching



Initial NONreducing unit

Separation

AMYLOSE - AMYLOPECTIN 2

- Selective enzymatic BREAK DOWN **AMYLOPECTIN to Saccharide**
- Different Solubility of the **AMYLOPECTIN** and **AMYLOSE**
  - **Mixture of DMSO + Water > Different Solubilities**
  - **Water + NaOH > salt out by NaCl > AMYLOSE in the Solution and AMYLOPECTIN forms the Gel (Separation takes a longer time)**

Isolation (Separation) of AMYLOSE and AMYLOPECTIN
Laboratory instructions

Principle

Starch is a universal storage Polysaccharide of Plants. It is present in the Form of Starch grains there. There is high Concentration of the Starch in some parts of Plants (Potato tuber, Corn Grain etc.). The Grains are formed from two Structures. AMYLOSE - linear polymer and AMYLOPECTINE - branched polymer. These Polymers is possible to separate on the basis of their different Solubility

Isolation (Separation) of AMYLOSE from AMYLOPECTIN

Pour to the Beaker of Volume 1000 cm^3 360 cm^3 0,2 $mol.dm^{-3}$ of the NaOH solution in Water, 75 cm^3. Add 5,3 g of the dry Starch mixed in 35 cm^3 in Water and at Temperature 25 °C mix (stir) by glass Stick up clarifying the Solution. Add 125 cm^3 of the NaCl Solution (5 % w/w) and neutralize by HCl Solution up to pH 6 – 7. Check the pH Value by test paper. Leave the system stay at laboratory Temperature 20 hours, avoid Sun light. **AMYLOPECTIN** is separated on the Bottom as the Gel, **AMYLOSE** remains in the Solution.

It is possible to call this as the „SALT OUT “. It is visible influence of ions on the polymer solubility.

REMARK: The separated AMYLOPECTIN is possible filter out and AMYLOSE precipitate as the Complex with Butanol. Add 12,5 ml of Butanol to 100 cm^3 of the **AMYLOSE Solution and leave it stay for 2 hours.**

AMYLOSE & AMYLOPECTIN 3
SIMILARITY TO Polyethylenes

LDPE

- **Branched**
- **Higher Melt elasticity**

HDPE

- **Linear**
- **LOWER Melt elasticity**

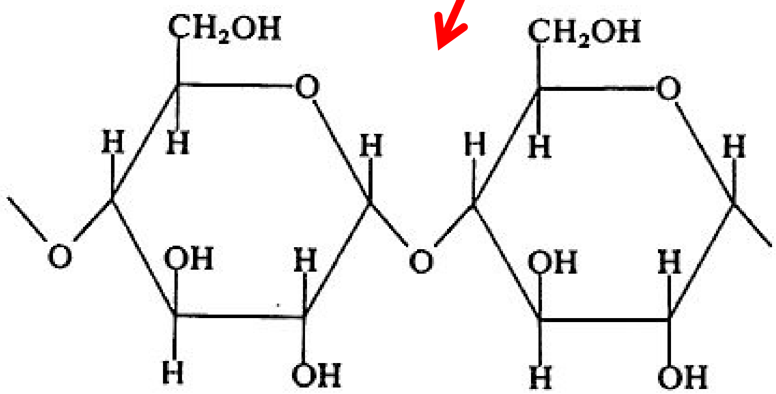
AMYLOPECTIN

- ***Branched***
- ***Higher Melt elasticity in the Mixture of Starch - Glycerol***

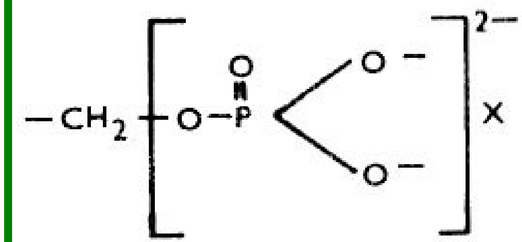
AMYLOSE

- ***Linear***
- ***LOWER Melt elasticity in the Mixture of Starch - Glycerol***

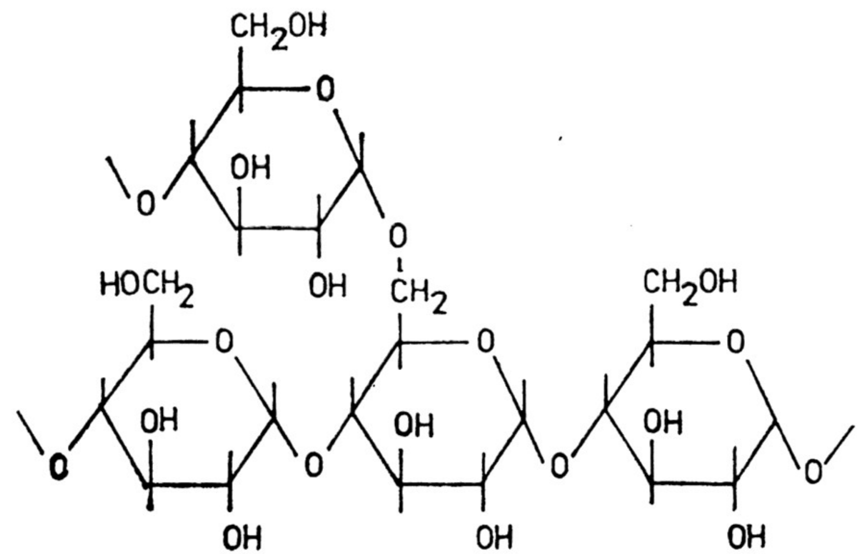
AMYLOSE - AMYLOPECTIN 4



poly(1→4)-α-D-gluko-pyranosa (amylosa)



The Orthophosphoric acid could be bound on AMYLOPEKTIN, especially in the Potato starch.
The Cations (K^{+}, Ca^{+2}, Mg^{+2} etc.) have then influence on the Viscosity of the Water solutions and/or Gels.



(1 → 6)-α-D-glukopyranosyl-D-glukosy

AMYLOSE - AMYLOPECTIN 5

Properties Comparision of AMYLOSE - AMYLOPECTIN		
Property	**AMYLOSE**	**AMYLOPECTIN**
Complex with I^{-1} Colour	Blue	Red-vilolet
Relative MW	$10^3 – 10^6$	$10^7 - 10^8$
Crystallinity by RTG Diffration	High crystallinity	Amorphous
Solubility in Water	Different	Soluble

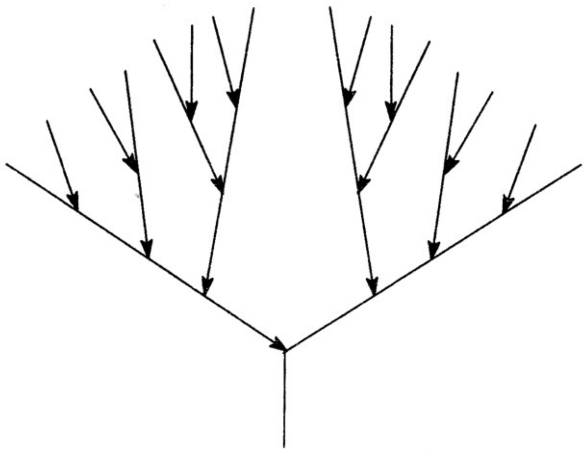
According to Literature: Radley, J.A. (Editor): Starch and its Derivatives, Chapman and Hall, London 1968

AMYLOSE - AMYLOPECTIN 6

Relativ Average molar mass (MW)	AMYLOSE	AMYLOPECTIN	Source, Remark
M_n	$10^5 - 10^6$	10^7	**Czech Texbook**
M_w			***It was not found***
M ??? n or w	$10^5 - 10^6$	$10^7 - 10^8$	**Czech Book**

Any case, these Figures are HIGH, at Level (Rank equally) Synthetic polyolefis (PE, PP)

AMYLOSE & AMYLOPECTIN 7



A possible structure of the **AMYLOPEKTIN** branching

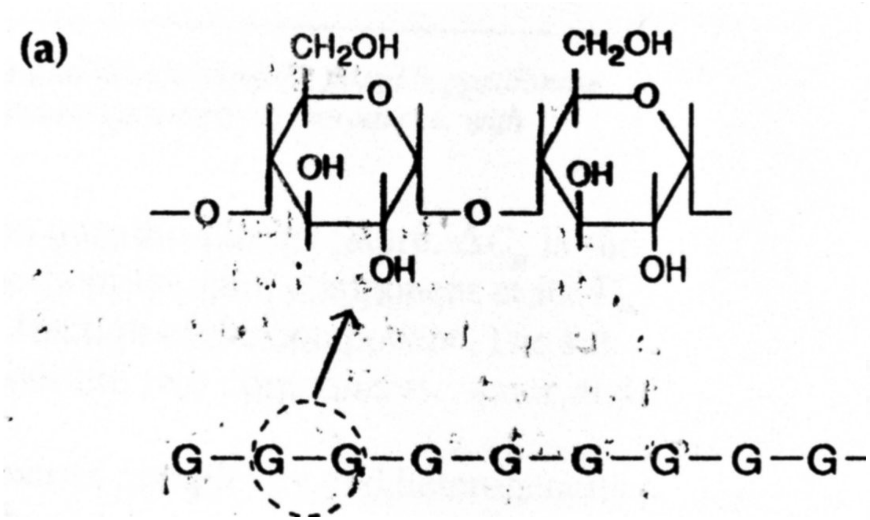
This Picture concerns WATER SOLUTIONS!

	AMYLOSE	AMYLOPECTIN
Bond type	α(1→4)	α(1→4) and α(1→6)
Morphology	Crystalline	Amorphous, alternatively partly
RETROGRADATION	Considerable	Low

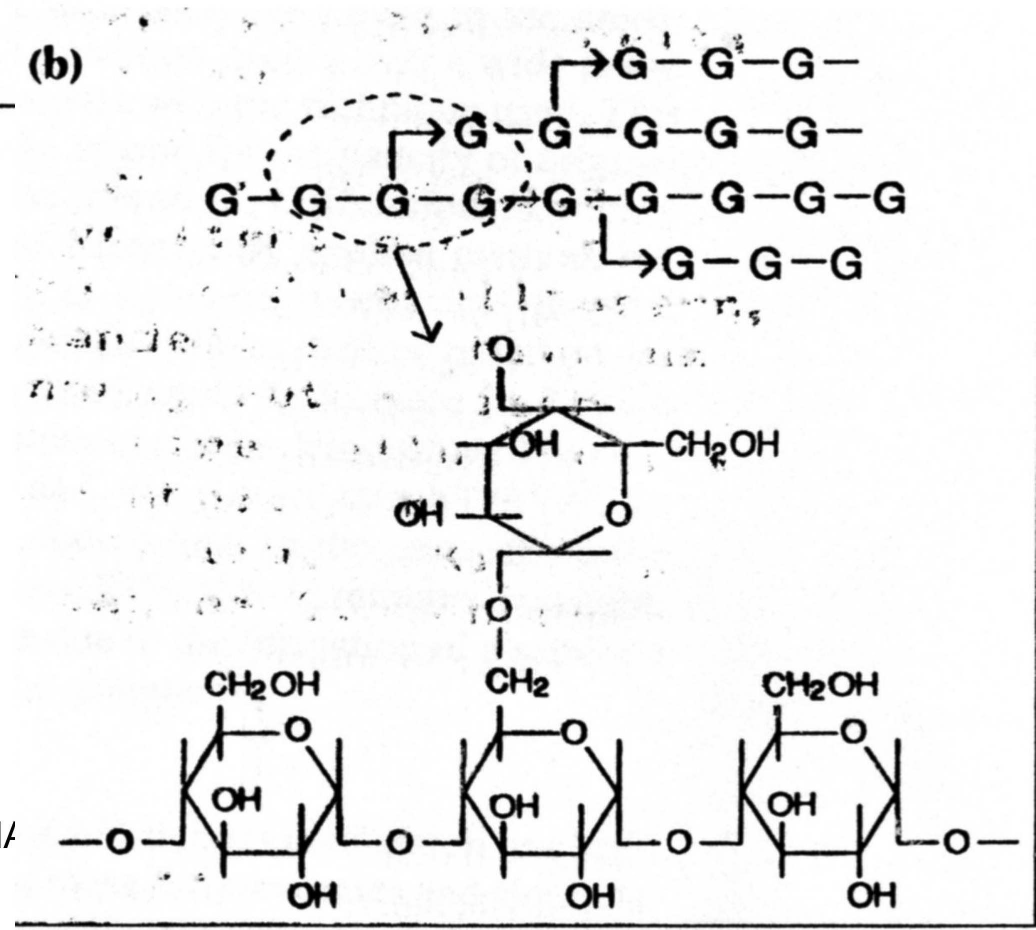
RETROGRADATION = from a Gel and/or Solution is precipitated POLYMER

AMYLOSE & AMYLOPECTIN 8

(a)



(b)



G – glucose unit

AMYLOSE & AMYLOPECTIN 9

- **AMYLOPECTIN usually prevails in Ratio 4/1**
- **AMYLOPECTIN does not give BLUE Colour with Iodine**
- **Some Starches, e.g. Pea Starch, contain AMYLOSE only**
- **The other Starches, e.g. Corn cultivar called Waxy Corn (Maize), have MYLOPECTIN only**
- **AMYLOPECTIN has higher MW**
- **………………….**

Starch MWD 1 (method GPC)

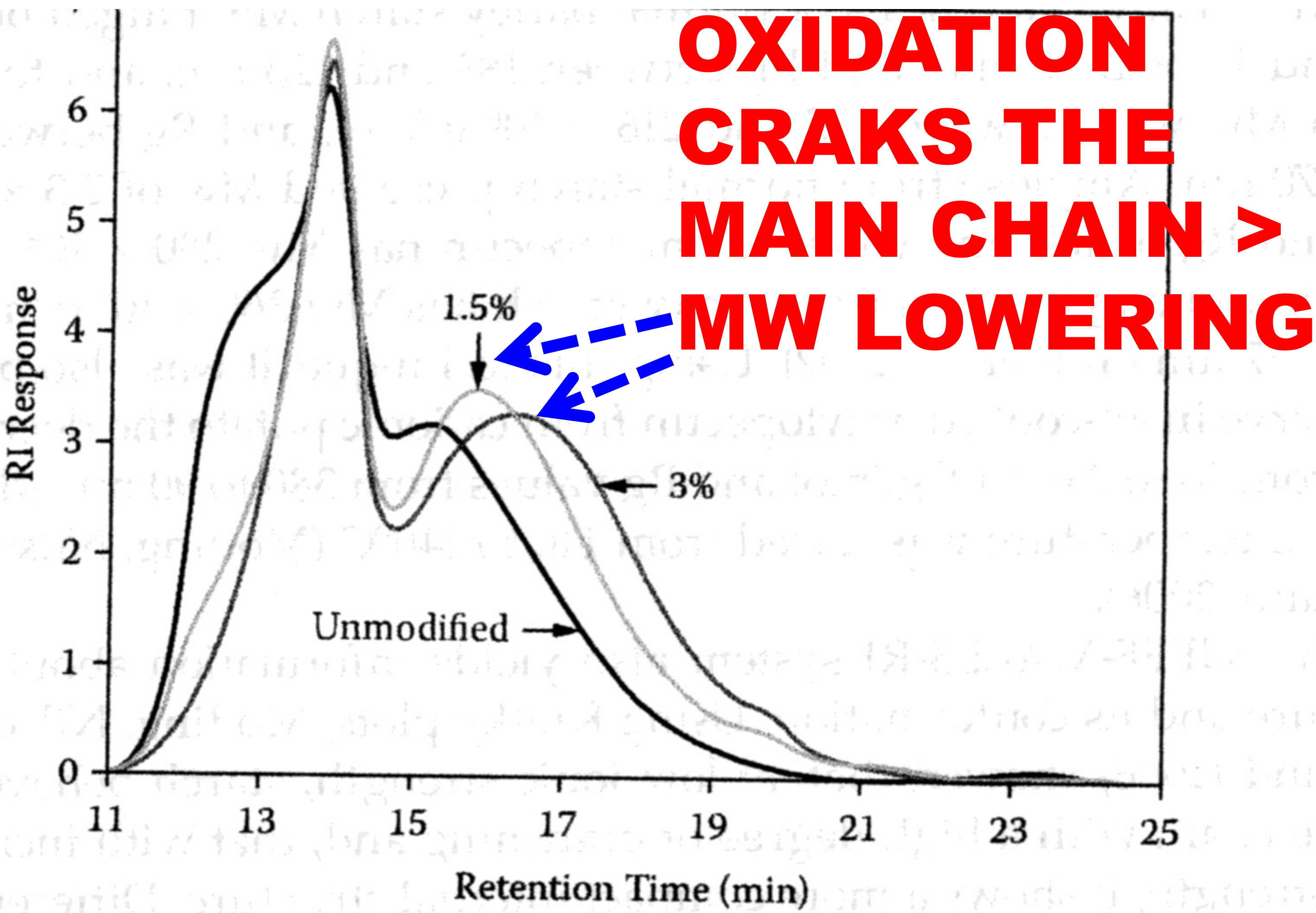
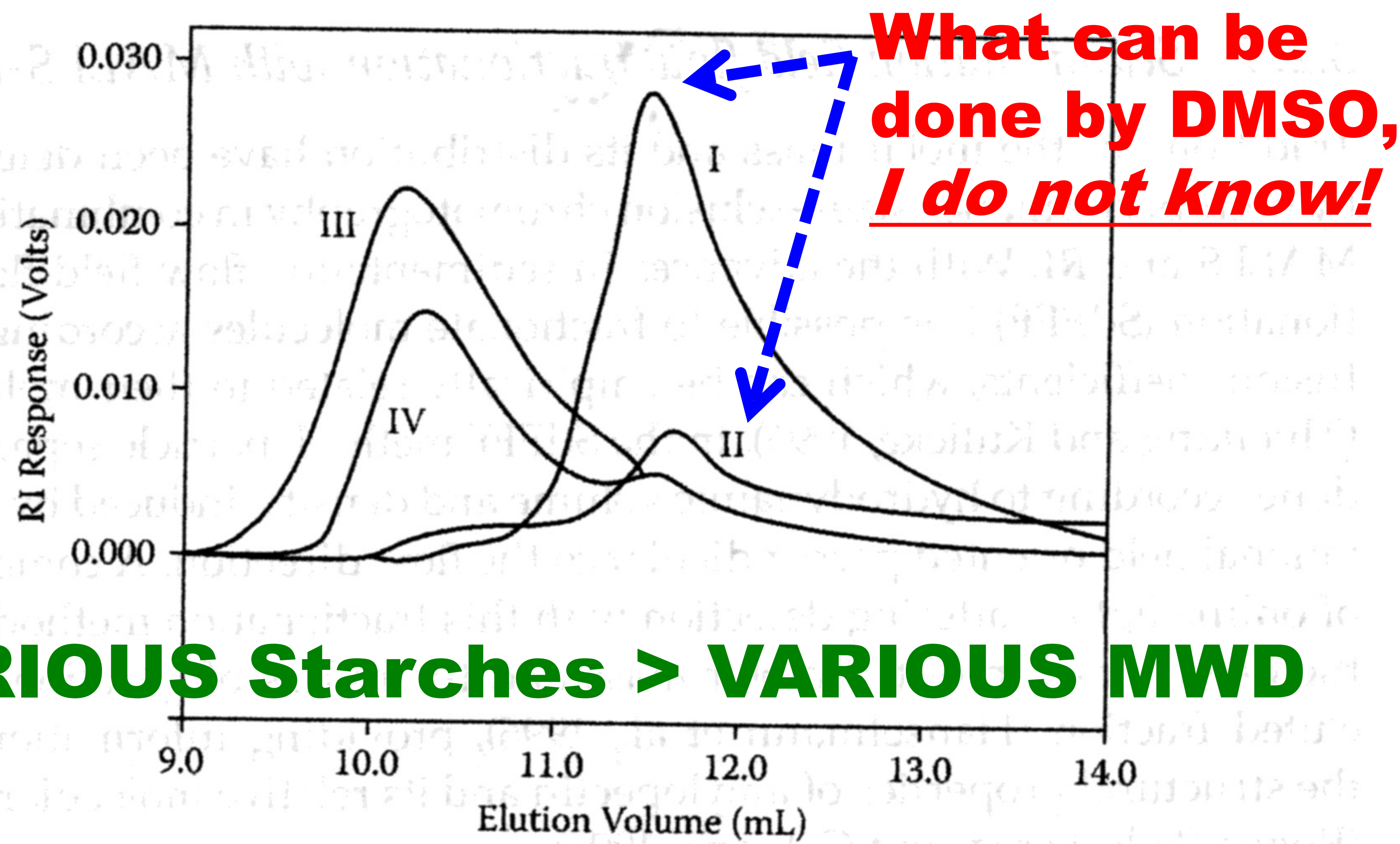


Figure 3.4 Normalized high-performance size-exclusion chromatographs of unmodified and oxidized starches (1.5 and 3% active chlorine).

Starch MWD 2 (method GPC)

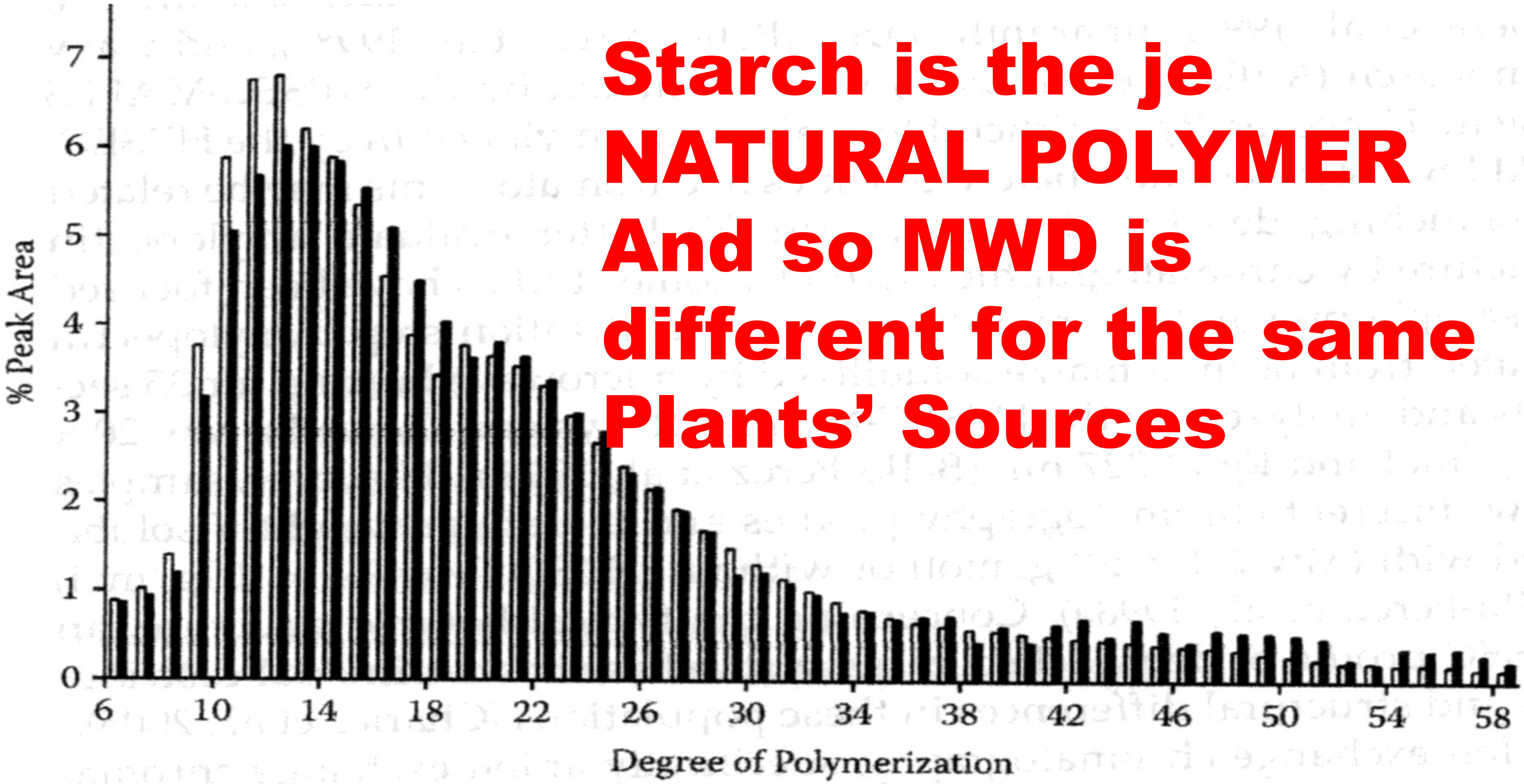


VARIOUS Starches > VARIOUS MWD

Figure 3.3 HPSEC profiles of starch from amylose of maize treated with DMSO (I), amylopectin maize (II), normal maize (III), and Eurylon 7 starch (IV) (Bello-Perez et al., 1998a).

Starch MWD 3

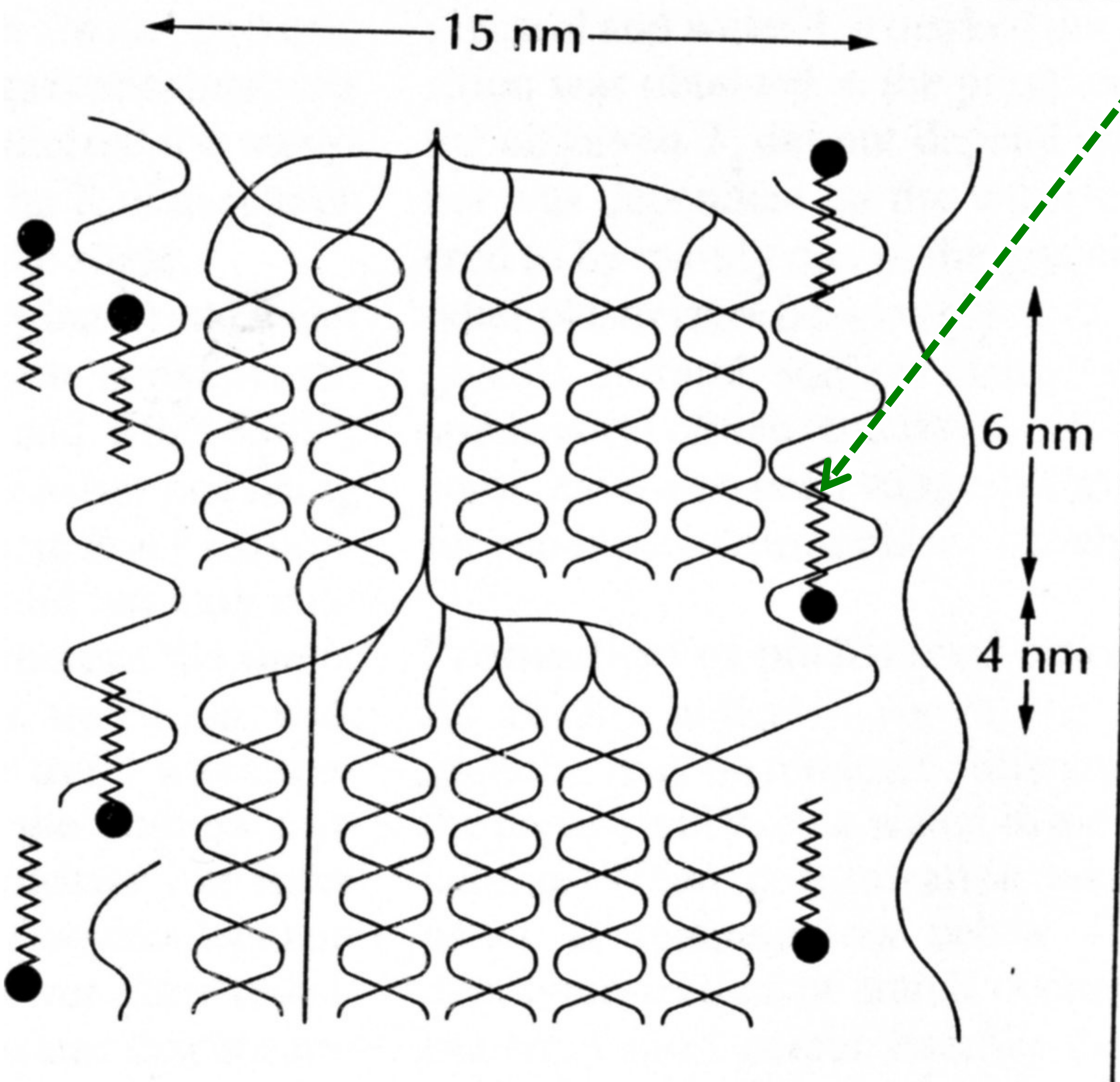
VARIOUS Starches > almost the Same MWD



Starch is the je NATURAL POLYMER And so MWD is different for the same Plants' Sources

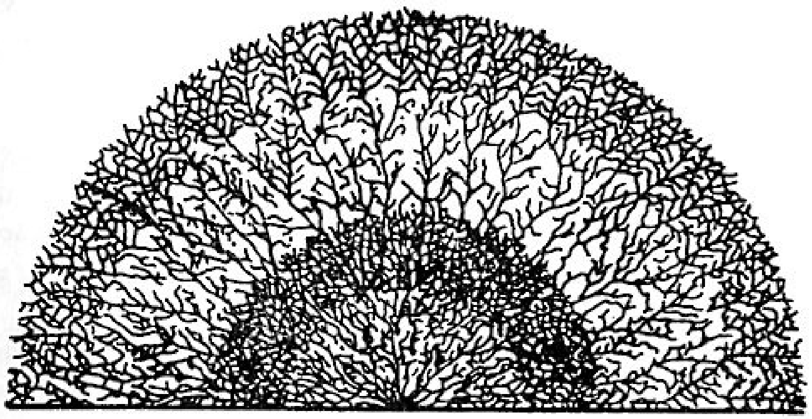
Figure 3.5 Amylopectin chain length distribution of normal maize (□) and barley (■) starch, measured by high-performance anion exchange chromatography (HPAEC) with pulsed amperometric detection (PAD).

Possible deposition of the Fats molecules in the Cereal Starch



I do not like this Scheme, because Fats are TRIGLYCERIDES and here is only one Helix! There is not enough Space in the Helix of Amylose!

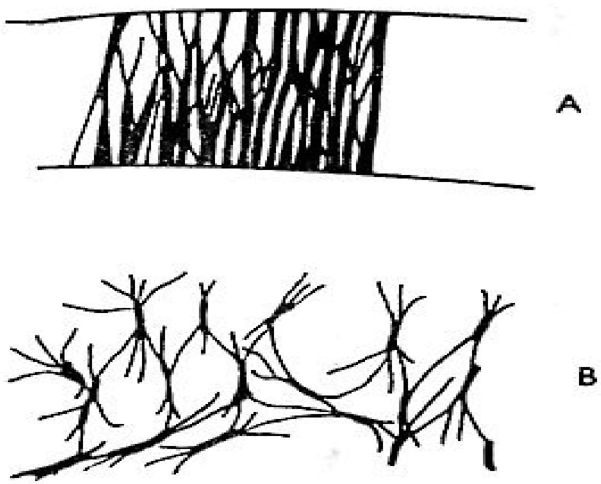
SUPRAMOLECULAR STRUCTURE of STARCH



Spherollitic Structure of the Starch Particle

Linear **AMYLOSE – Crystallize** via Hydrogen bond
Branched AMYLOPECTIN – the only enough long Branches can **Crystallize.** The Basic chain can go trough many such **Crystalline parts.**

Crystalline parts are permeated by and connected by Amorphous parts (NONCrystalline), as it is in synthetic SEMIKRYSTALLINE polymers



SUPRAMOLECULAR Structure of the Starch Particle according to Meyer:

a) Structure of the Starch layer
b) Framework of the branched part after Washing out the Amylose