Beer Stability and Stabilization

Different Terms of Stability in Beer

- Microbiological stability: Absence of any critical germ in the beer, e. g. spoilage bacteria
- Non-biological stability: Resistance of a beer against haze formation that is not originated from microbiological contaminations (→ raw materials)
- Flavor stability: Ability of the beer to keep its fresh, pure flavor as long as possible after filling; stability against the formation of stale flavor carbonyls
- Foam stability (head retention): Ability of the beer to keep the head as long as possible

The non-biological turbidity dealt with in modern stabilization practices is known as „colloidal haze".

Evaluation of the clarity of a beer

Turbidity in EBC-Units	EVALUATION
< 0,2	CLEAR AND SHINY
≤ 0,3	minimum value for a filtered beer
0,2...1,0	Clear
1,1...2,0	slightly opal
2,1...4,0	Opal
4,1...8,0	Turbid
> 8,0	very turbid

What is colloidal Haze?

- Caused by low molecular weight polyphenols cross-linked with proteins by weak molecular interactions, such as hydrogen bonds. (protein-polyphenol haze)

- Colloidal haze is often formed during cold fermentation and storage and is usually removed during clarification/filtration.

- The reactions between proteins and polyphenols can continue after filtration if sufficient quantities remain!

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Composition of Beer Hazes (Literature Values)

Polypeptides [%]	Polyphenols [%]	Polysaccherides [%]	Mineral-compounds [%]
58-77	15-77	2-13	2-14
40-76	20-55	-	-
65	-	35	-
45-67	20-30	-	-
40-46	-	2-4	1-4
14-45	1-3	40-80	-
-	-	40	-

Anger, Brauwelt Int. 1996

Protein Fractions in Beer and their Tendency to form Turbidity

Molecular weight of beer proteins [Dalton]	Average concentration in beer [%]	Correlation factor [-]
> 75 000	2	0,95
35 000...75 000	8	0,93
13 000...35 000	7,5	0,74
10 000...13 000	22,5	0,45
< 10 000	60	-

Source: Mussche, De Pauw: J. Inst. Brewing **1999**

Polyphenols

- Important part in haze formation
- Contribute to colloidal instability by protein precipitation
- Ability to form complexes with protein
- Tannins ➔ flavanoids ➔ dimeric, trimeric, oligomeric proanthocyanidins

Flavanoids

- Flavanols (=catechins) and flavandiols (=leucoanthocyanidin) ➔ called **flavanoids**
- Flavanoids are able to polymerize to polymeric molecules (never in beer, like formerly claimed, this only happens during the biosynthesis of the plants)
- Polymeric flavanoids are also known as condensed tannins or proanthocyanidins
- Important proanthocyanidins based on catechin, epicatechin, gallocatechin and epigallocatechin

Phenols

Polyphenole

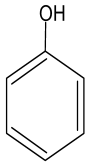
"Total Polyphenoles"

Phenolcarbonic acids

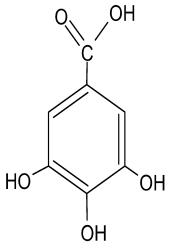
Catechine (Flavanoide)

Anthocyanidine

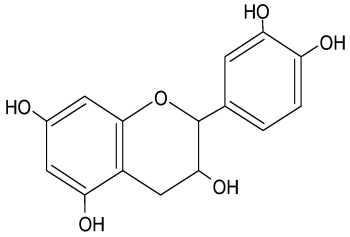
Flavonoide



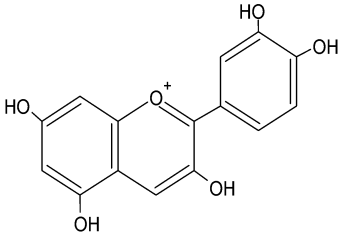
Phenol



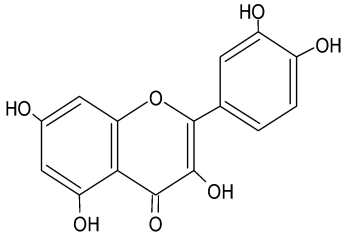
Gallussäure



Catechin



Cyanidin

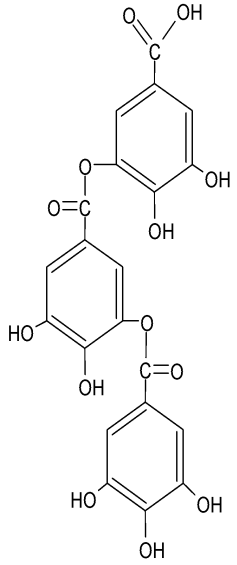


Quercetin

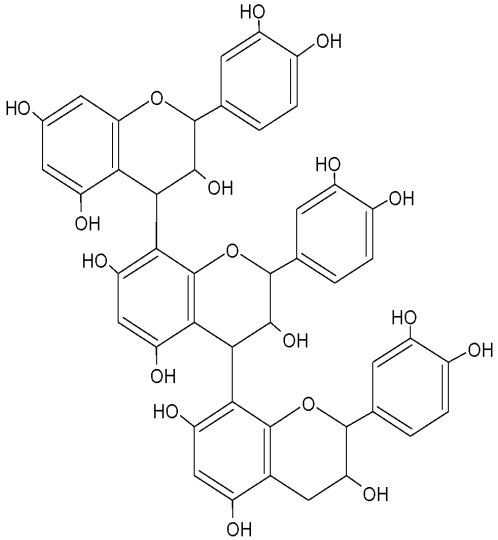
"Anthocyanogene"

Proanthocyanidine/Tannine "Tannoide"

"Echte" (Gallo) tannine

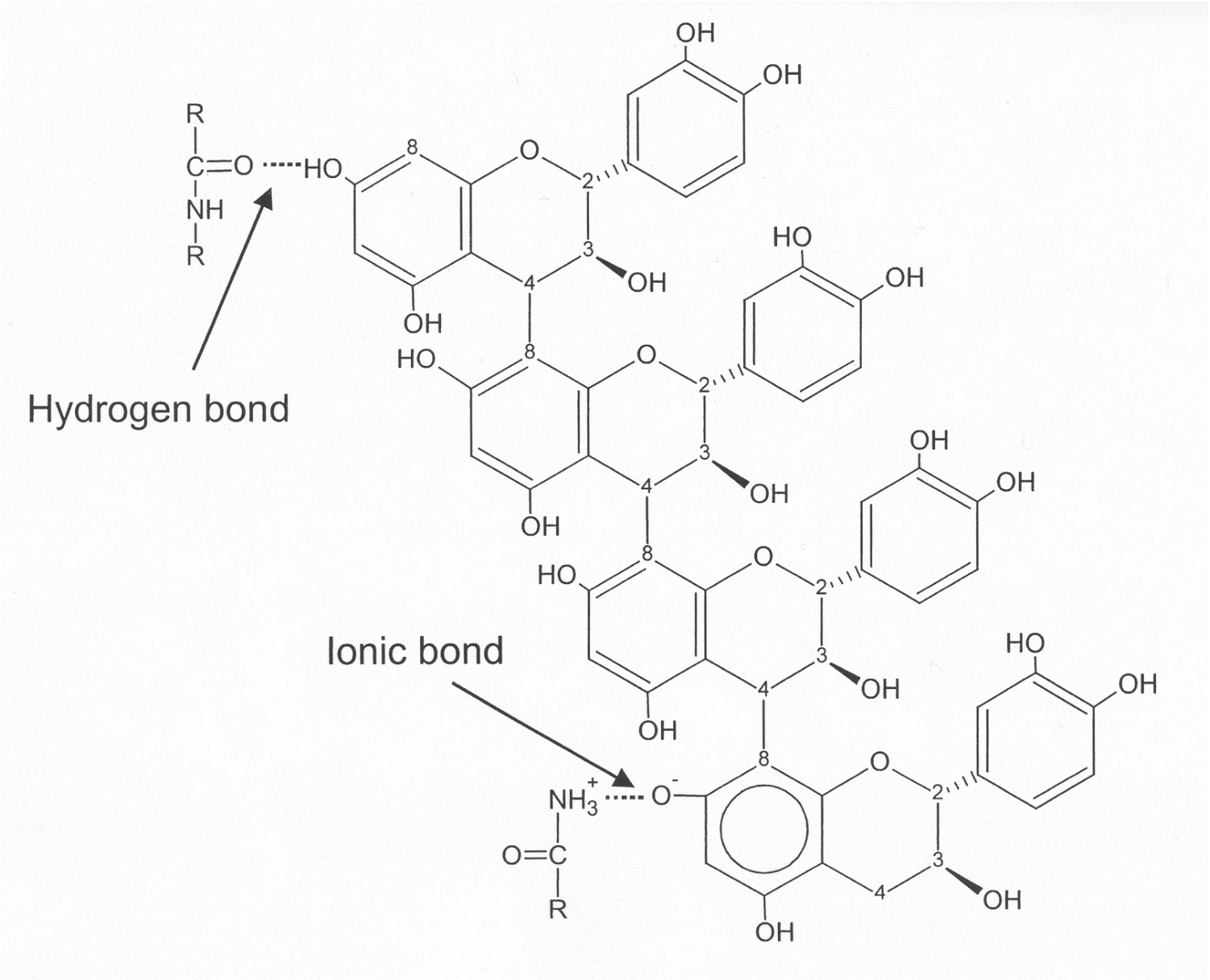


Tanic acid

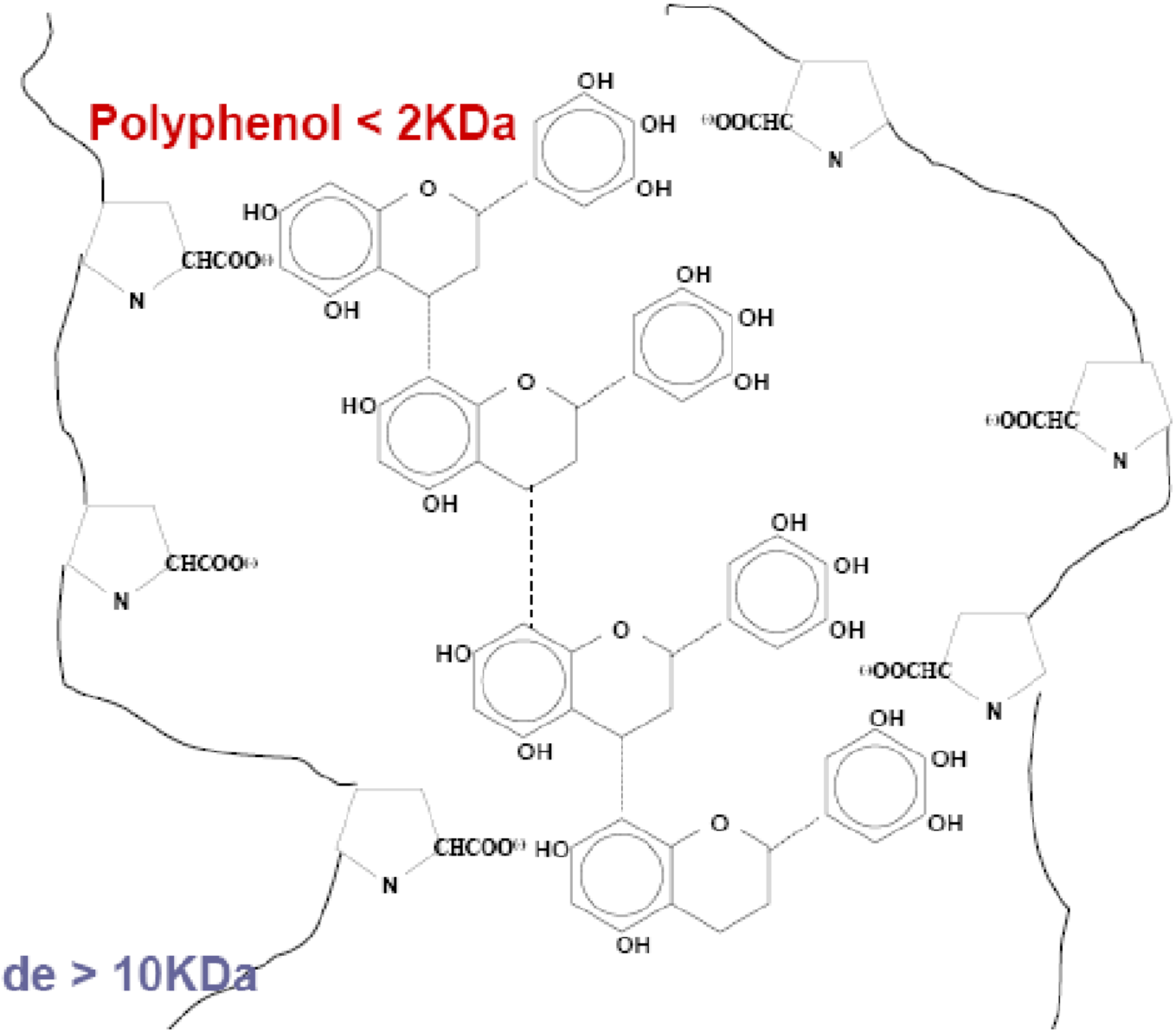


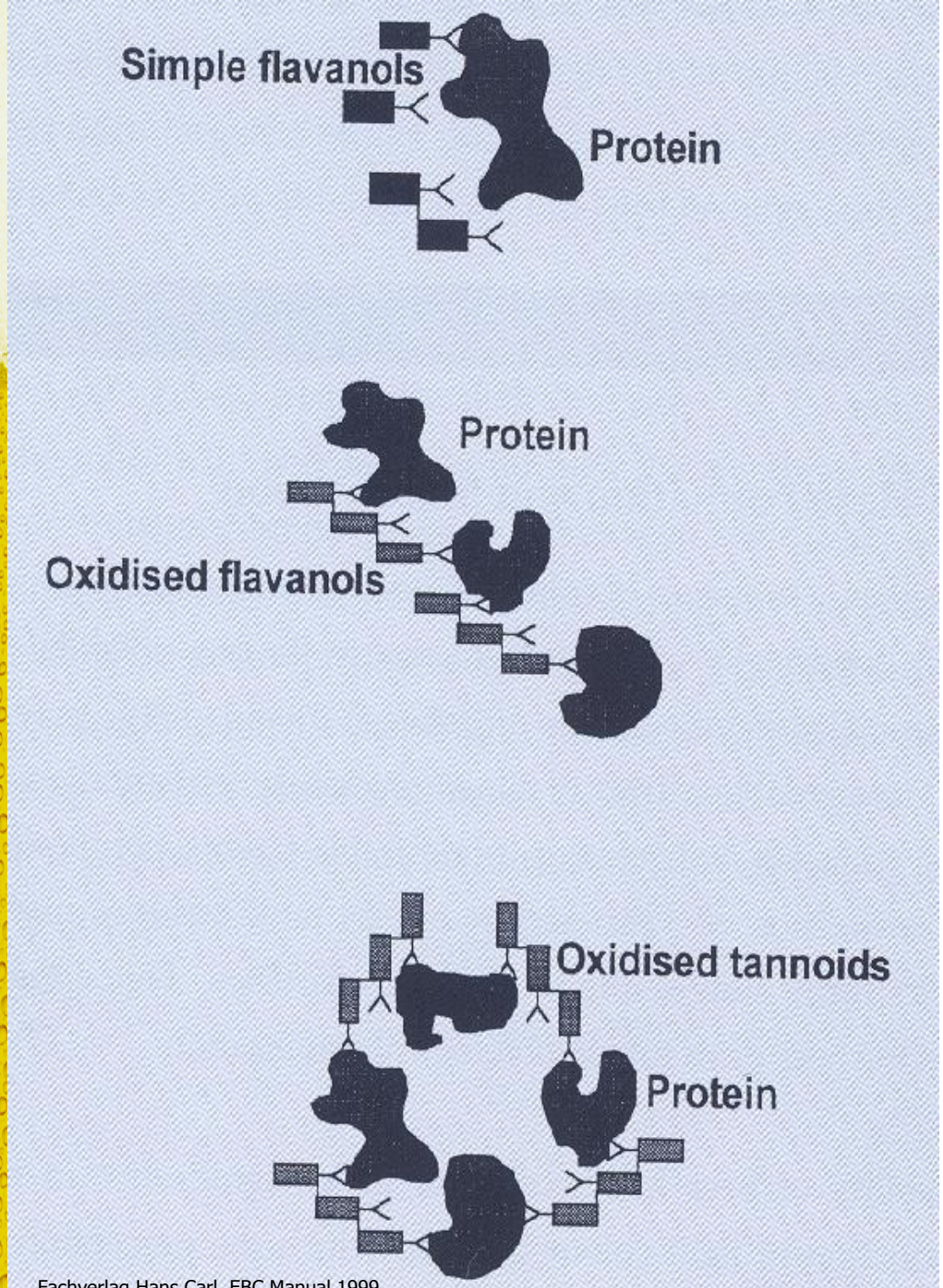
Trimeric Procyanidine

Tannin – Protein – Complex



Protein – Polyphenol Interaction





Model of colloidal Haze Development

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Fachverlag Hans Carl, EBC Manual 1999

Chill haze

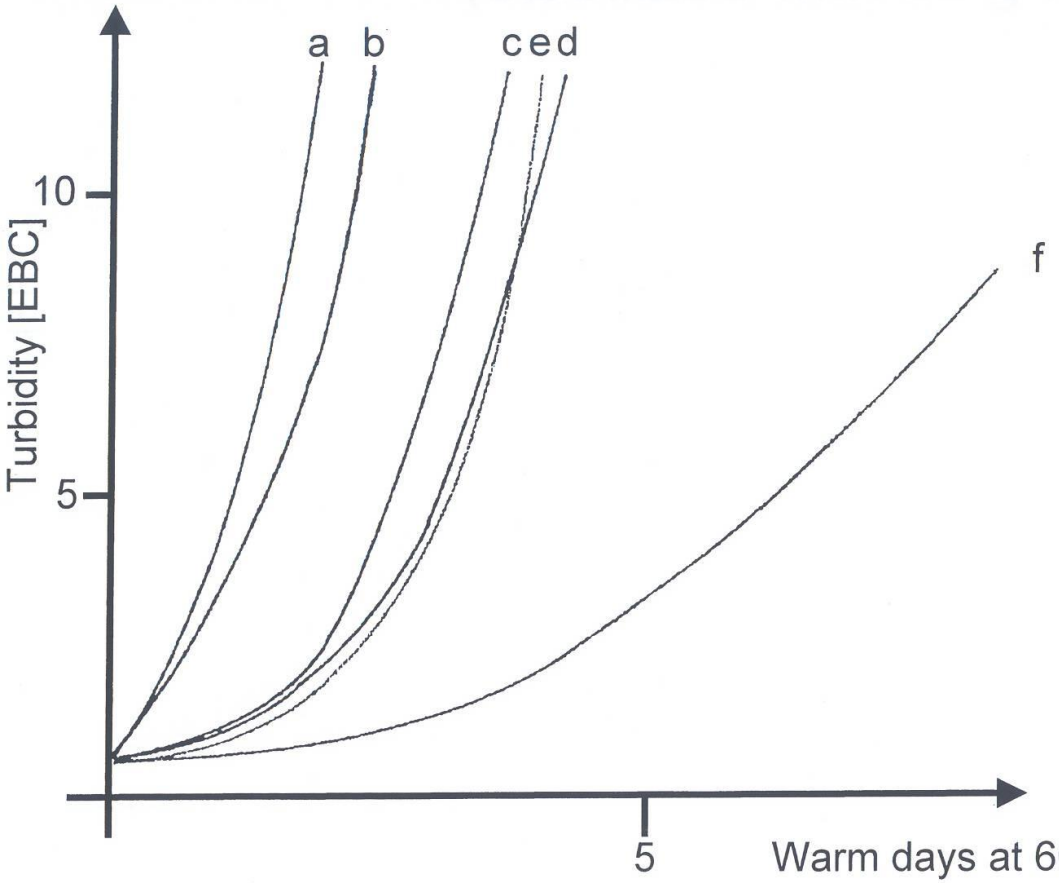
- Chill haze is reversible
- Haze disappears at higher temperatures after having been formed at about 0 °C
- Beers maturated and filtered at a temperature below 0 °C do not form chill haze at the beginning
- After extended time at higher temperatures on the shelf beer becomes sensitive to cold
- After a while, chill haze is converted into permanent haze

Methods of Stabilization

The primary methods available to control haze are based on the following chemical interactions:

- Adsorption
- Precipitation
- Enzymatic hydrolization

Stabilization by cold Storage



	Storage time	Temperature
	[days]	[°C]
a	0	10
b	0	5
c	0	0
d	2	0
e	4	0
f	8	0

Stabilization by cold Storage

0 °C - storage		4 days	8 days	14 days
Original gravity	[°P]	12,9	12,9	12,9
colour	[EBC]	9,6	9,2	9,1
Foam stability (R & C)	[Σ]	124	121	121
Warm days at 60 °C	[Tage]	2,7	3,6	4,7
Total N	[ppm]	939	932	920
Coagulable N	[ppm]	12	9	8
$MgSO_4$-precipitable N	[ppm]	175	171	173
Dimeric Proanthocyanidine	[ppm]	8,1	8,7	8,3
Catechine	[ppm]	21,5	18,0	17,5
Tannic acids	[ppm]	20,8	21,3	15,9
Anthocyanogene	[ppm]	28,0	29,9	24,2
Total-Polyphenol	[ppm]	144	134	131

Impact of Lager Temperature (7 days) on colloidal Stability

Temperature	4 °C	2 °C	0 °C	-2 °C
No. of warm days (60 °C)	1,0 days	1,6 days	1,8 days	4,0 days
Foam stability Ross & Clark	118 sec	119 sec	121 sec	123 sec

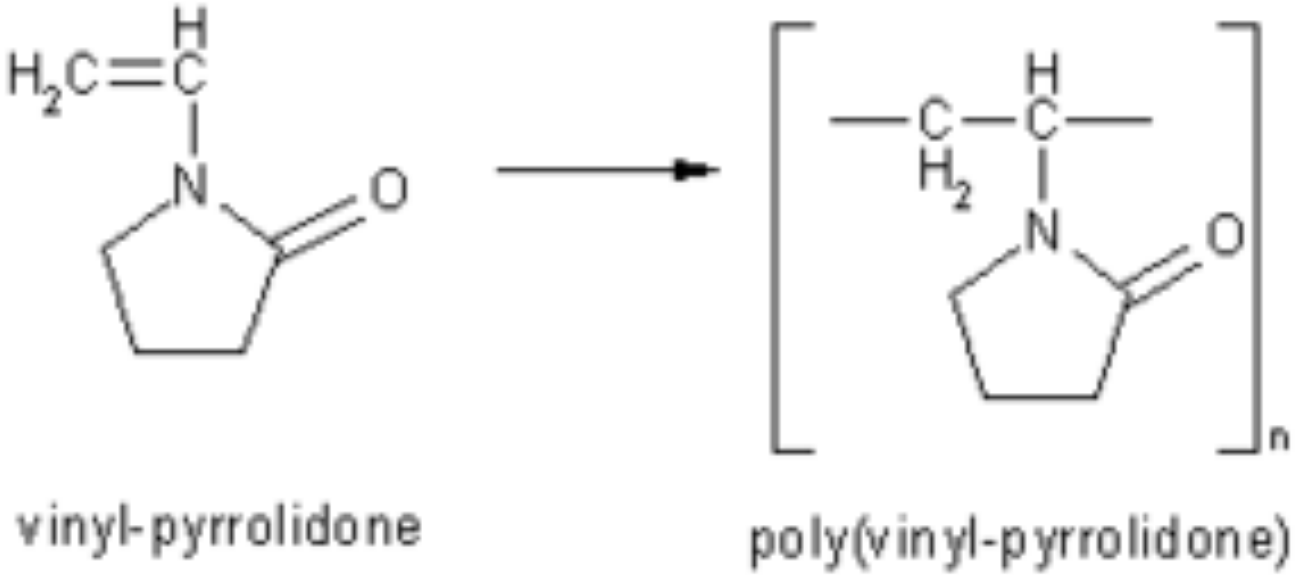
Methods of Stabilization

Given that the primary cause of non-biological beer haze is protein-polyphenol haze, modern stabilization methods attempt to remove either one or even both of the two reactive partners of the reaction.

- Proteins of molecular weight of ca. 40000 D
- Polyphenols

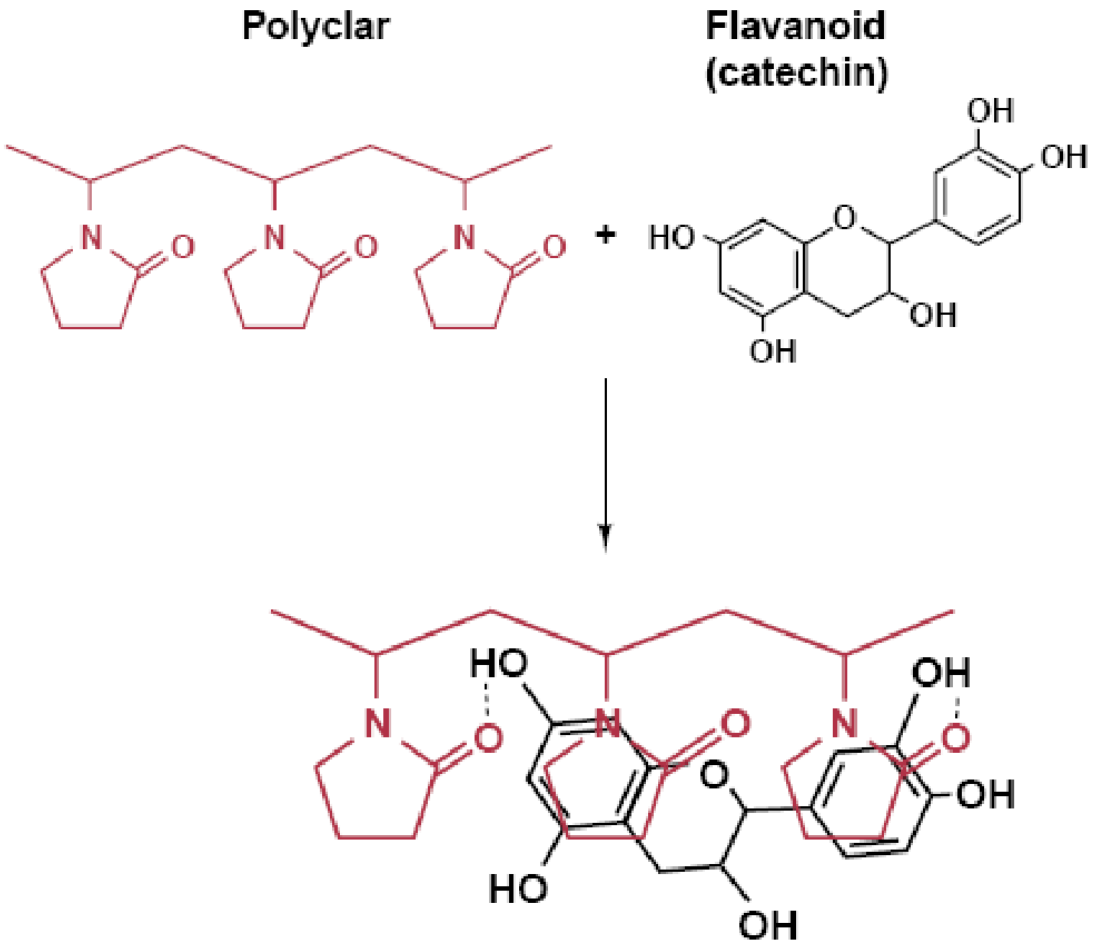
The two main compounds which are used to adsorb these molecules are PVPP and Silica Gel.

PVPP - *(Polyvinylpolypyrrolidone)*



- Non-soluble in water
- PVPP (Polivinylpolypyrrolidone): polymer of vinylpyrrolidone
- Acts through the formation of hydrogen-bonds between its carbonyl group and the hydrogen atom of the hydroxyl group of polyphenols in acidic environment - has a similar structure to a high molecular proline containing protein → high affinity to polyphenols

Mechanism of Adsorption of Polyphenols using PVPP



ISP

Application of PVPP: Increased Stability by Removal of Tannins

PVPP [g/hl]	Proantho cyanidins [ppm]	Catechins [ppm]	$MgSO_4$- N [ppm]	Warm days 60°C [EBC]	Foam R&C [sec]	Colour [EBC]
0	5,4	8,9	177	0,5	125	10,1
30	1,3	3,4	175	2,7	124	9,6
60	1,0	3,0	177	3,1	124	9,5
90	0,5	2,3	172	5,0	123	9,3

PVPP Products and Application

Single Use PVPP

Advantages

- No extra filter system
- Stabilization of small batches
- Higher catechin adsorption due to smaller particle sizes

Disadvantages

- Continuous cost for single-use PVPP
- Good efficiency only after pre-clarification with a separator
- Effect on the filter life circle

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PVPP Processing, single use

Factor	Recommended specification
Water suspension, correct concentration	Between 8 to 12% w/v in deaerated water
Hydration time	1 hour for complete hydration (swelling)
Contact time, minimum	Less then 1 minute
Contact time, maximum	None, adsorption is reversible
Dosing into beer	Proportional inline dosing at between 10 and 50 g/hl as required
Mixing	Thorough mixing in-line with beer stream
Beer quality	Ideally a minimum of suspended solids. No detrimental effects. PVPP is removed by filtration

PVPP Products and Application

Regenerable PVPP

Advantages

- Low PVPP consumption (0.5-1 % loss)
- Full automation
- Good control of stabilization

Disadvantages

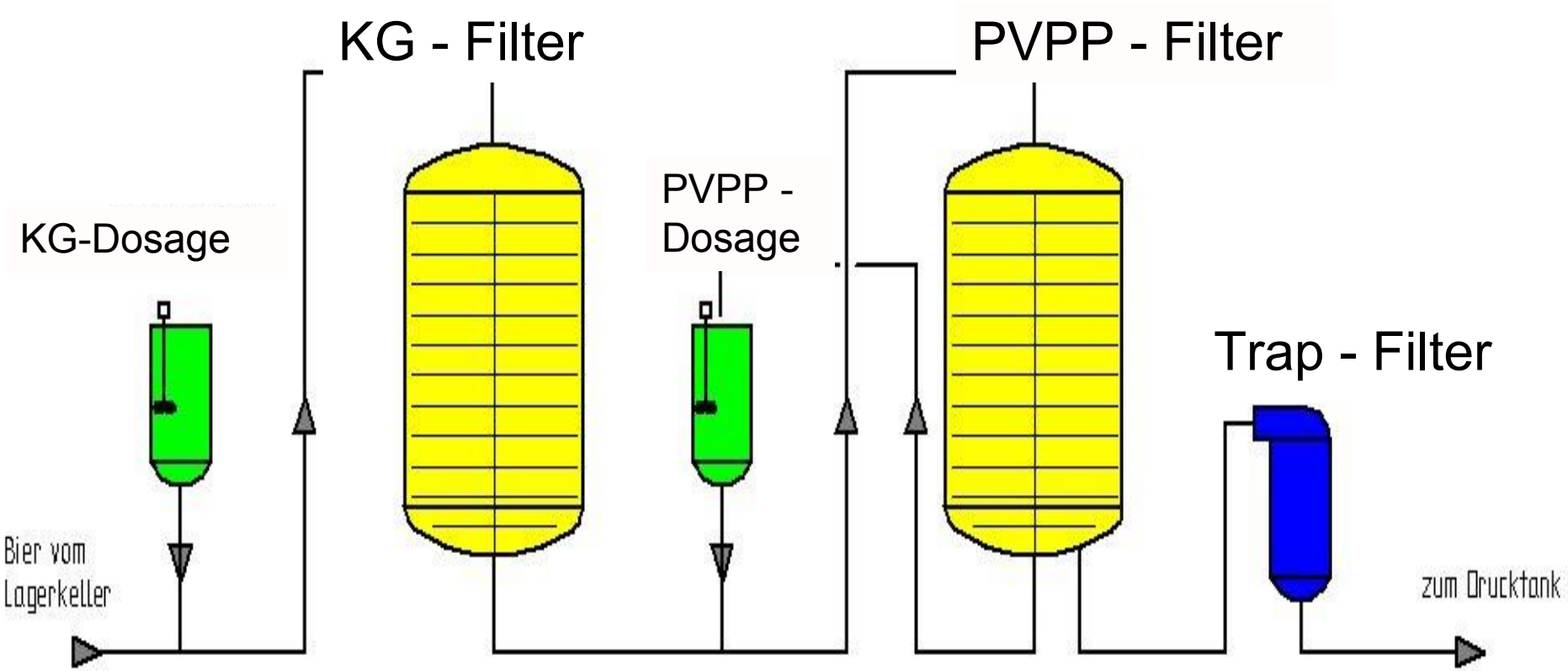
- Higher equipment costs due to separate PVPP filter and consecutive trap-filter

PVPP Products and Application

PVPP containing filter layers

- Regenerable filter layers with an average content of PVPP around 20 %
- Regeneration can be realized by the use of hot caustic and a following neutralization with acid
- Adsorptive effect of the filter layers decreases with the number of uses
- Blending might be necessary to obtain a homogenious beer quality

Filter Line with regenerable PVPP Filter



Named Advantages of the Use of PVPP

- Highly effective at relatively low dosage rates and with short contact times
- Consistently achieves maximum shelf-life in beer (allowing extended 'best before‘ date stamping)
- Easy to use with excellent handling characteristics
- No adverse impact on foam, flavour or other beer quality parameters
- No ldeclartion on abel required - completely removed by filtration
- Safe to use with no detrimental impact on the environment

Alternative PVPP Products

Crosspure®

- Regenerable PVPP for stabilization
- Polystyrene as filter aid

→ Combined two polymers offer filtration as well as stabilization in one process step

→ It is dosed like DE

→The regeneration of the product is comparable to that of PVPP with the difference that an additional enzymatic cleaning process step is required to digest the cell wall of the yeast cells

Source: BASF 2008: Crosspure - Information BASF

Silica Gel

- Used for the removal of haze protein fractions in beer by selective absorption. In general no influence on foam stability
- Can be added at different stages of the production process.
- Essentially two types of Silica Gels

  → Hydrogels with a total water content of < 60 %

  → Xerogels with a total water content of 5 %

  → Hydrated Xerogels with a water content of approx. 35 %

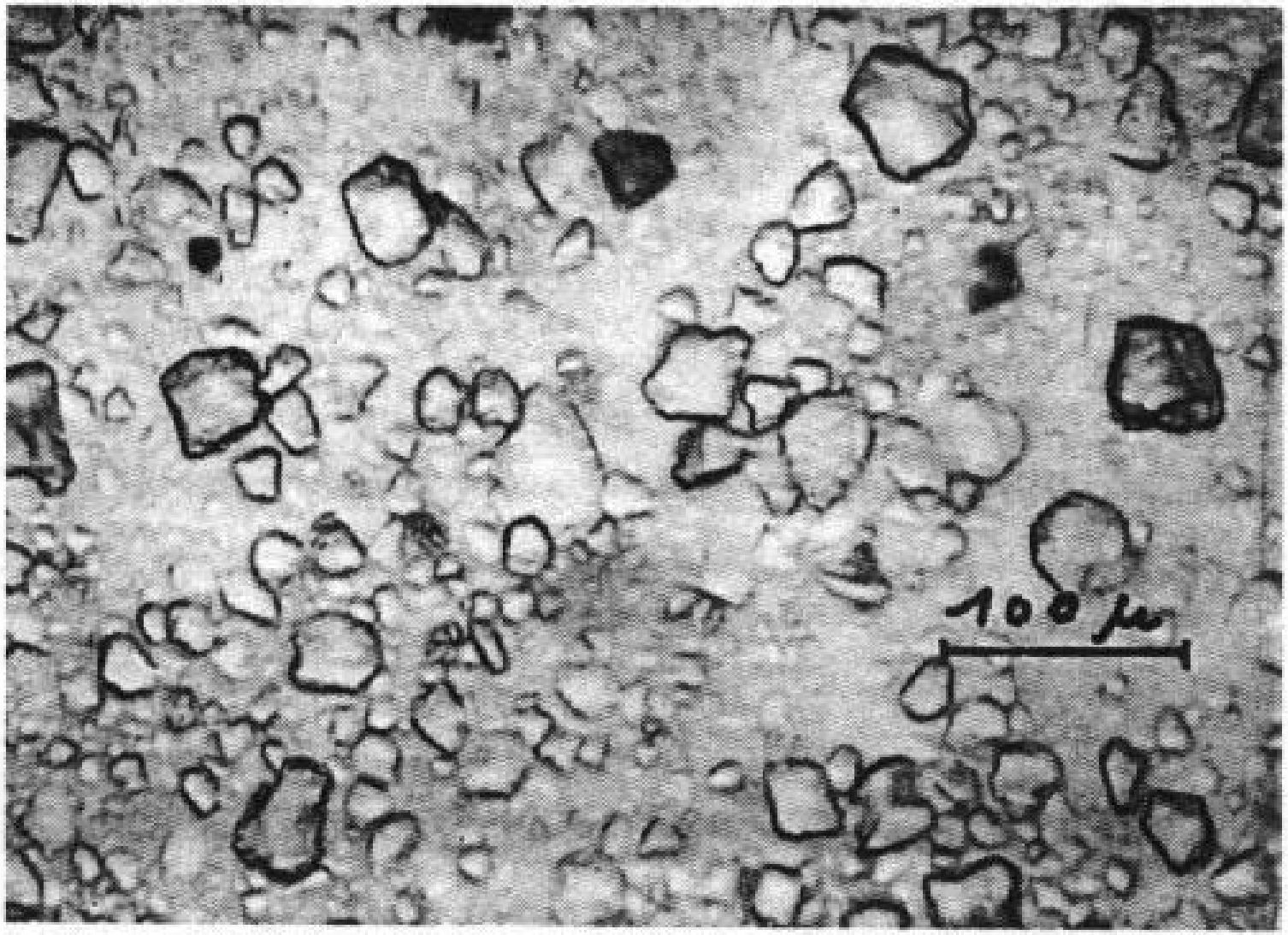
- By variations in the production process of the Xerogels influence can be taken on the fine structure of the gel and the inner surface (pore diameter)

Source: Marković, et al. (2003) - APTEFF, 34, 1–148

Silica Gel Parameters

	Hydrogel	Hydrated Xerogel	Xerogel
Solids	35 %	65 %	~ 90 %
Pore Volume	1.8-2.0	1.5	1.0-1.2
Surface Area	> 700 m^2/g	~550 m^2/g	~500 m^2/g
Pore Diameter	10-12 nm	10 nm	6-9 nm
Permeability	180-350 mDarcy	100 mDarcy	23 mDarcy

Silica-xero-gel 200x in light-microscope

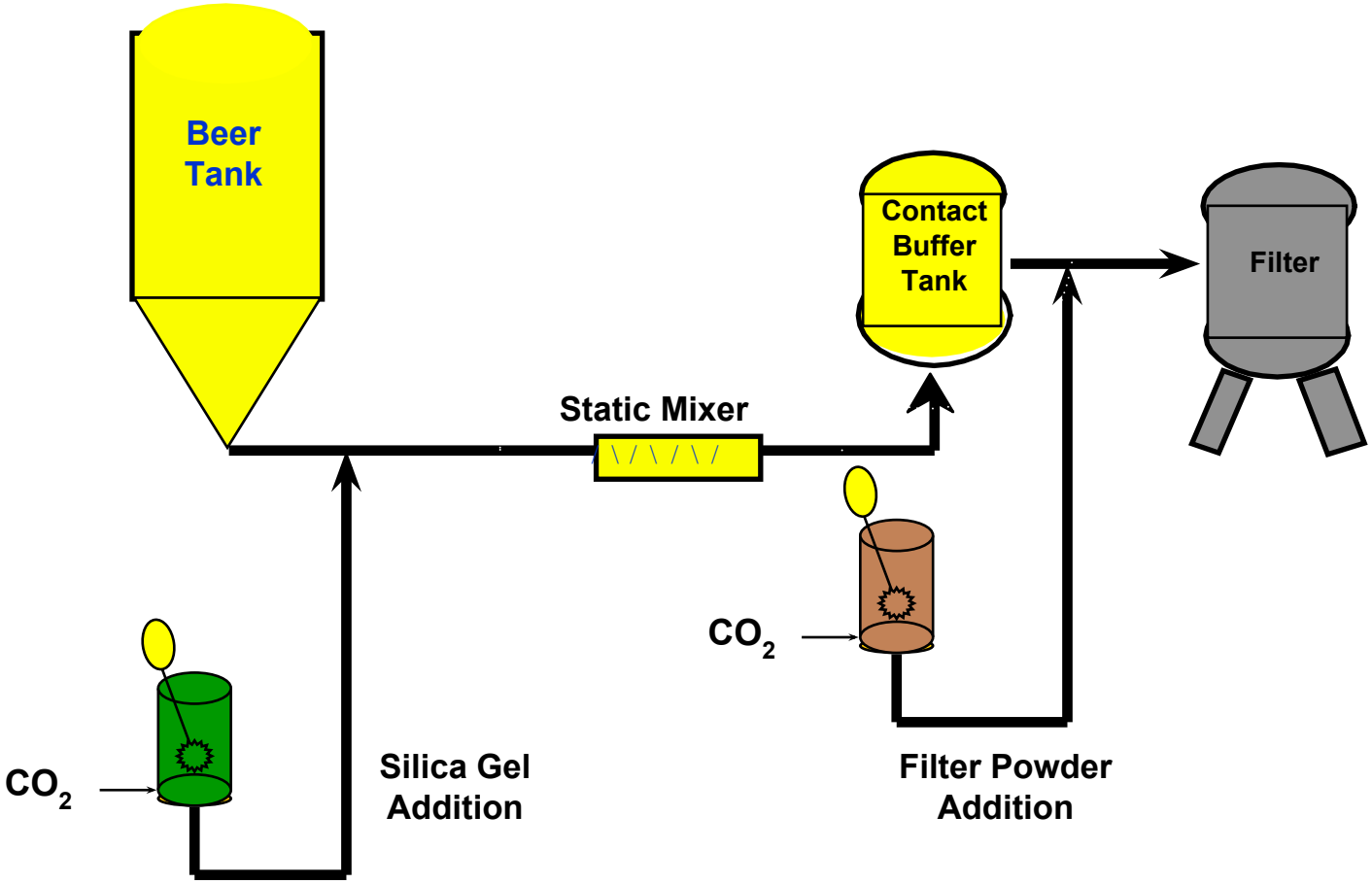


Silica Gel Dosing

- At the stage when green beer is pumped from the *fermentation tank* to the maturation tank
- To the *buffer tank* prior to DE filtration or centrifugation before using a cross-flow filtration unit
- Most often, silica gel is added together with DE or with single-use PVPP. When adding Silica Gel to the maturation stage, generally 1/3 of the total amount is added, while the remaining 2/3 are added at the filtration stage

Source: Marković, et al. (2003) - APTEFF, 34, 1–148

Application of silica gel as stabilizer to the Filter

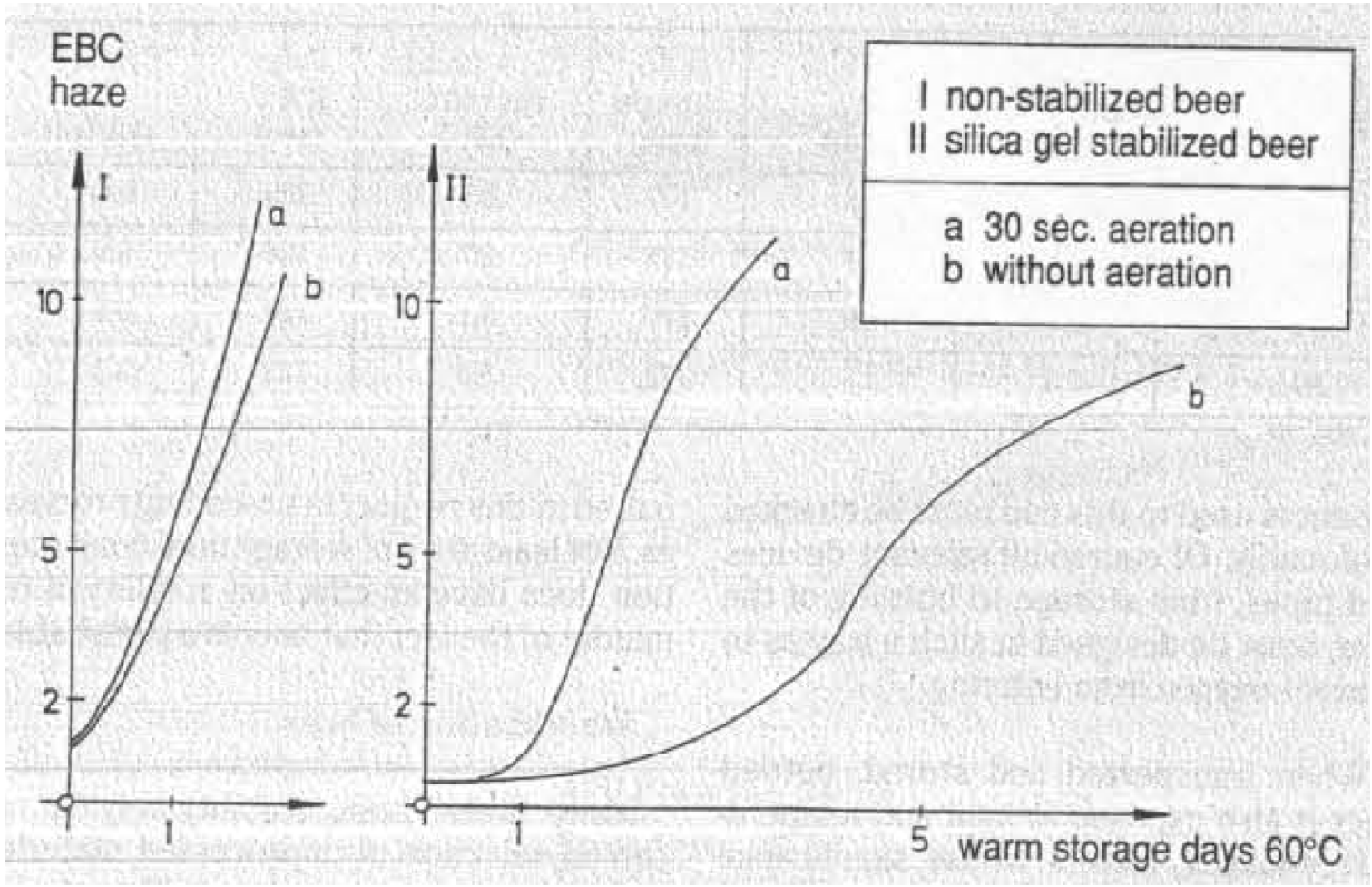


Source: PQ Systems

Application of Silica gel:
Increased stability by removal of protein and protein-tannin compounds

Silica [g/hl]	Proantho. [ppm]	Catechins [ppm]	MgSO4- N [ppm]	Warm days 60 °C	Foam R&C [sec]	Colour [EBC]
0	10,3	7,8	171	0,7	127	7,8
10	9,1	7,8	150	2,6	123	7,9
20	7,7	8,6	157	2,9	122	7,6
50	9,5	7,7	141	4,9	121	7,9

Anger, Brauwelt int. 1996



Anger, Brauwelt int. 1996

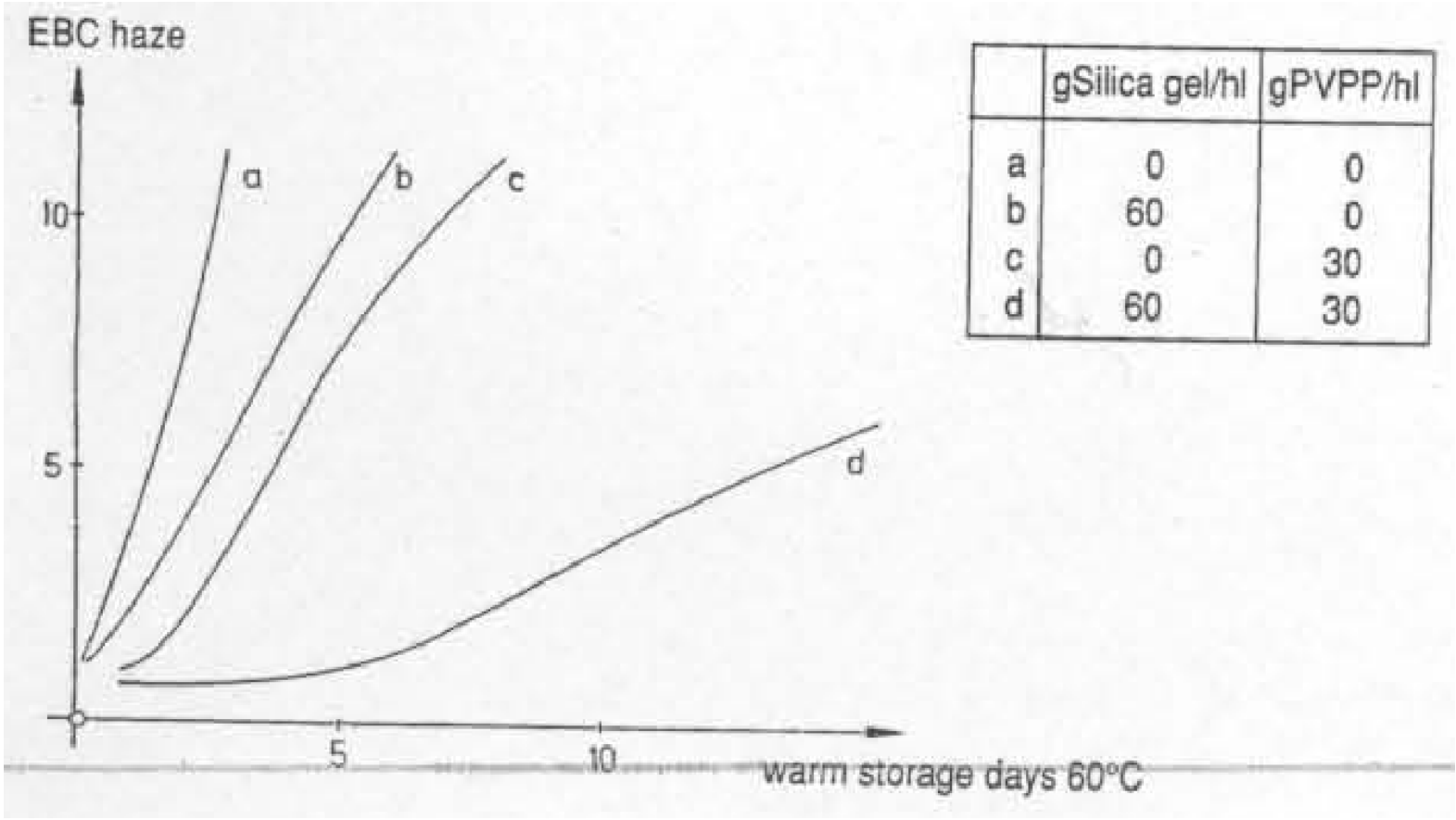
Combined PVPP / Silica Treatment

- Some studies claim that a balanced adsorption of protein and polyphenol is more desirable than removing either polyphenol or protein alone. Combined use of PVPP and Silica Gel have shown to give very effective stability.
- Composite products of Silica Gel and PVPP are available.
- It has been reported that the beer treated with the combined stabilizer gave lower filter differential pressure and a longer run

Table 3. Increase in filter run length with combined application of polyvinylpolypyrrolidone (PVPP) and silica gel as an admixture (Polyclar Plus 730)

Stabilizer	Addition rate (g/hL)	Δp/h	Filter run time (h)
Xerogel only	36	0.49	6.4
PVPP only	13	0.35	7.4
Polyclar Plus 730	33	0.25	12.0

Source: Rehmanji et al. (2005), MBAA TQ vol. 42, no. 4 • 2005 • pp. 335-337



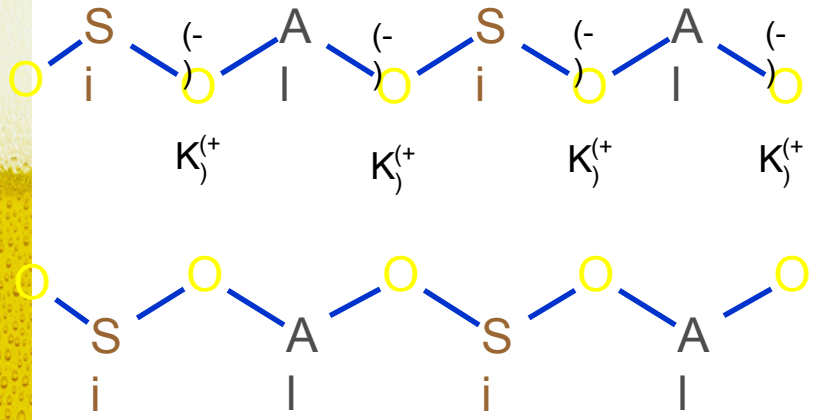
	gSilica gel/hl	gPVPP/hl
a	0	0
b	60	0
c	0	30
d	60	30

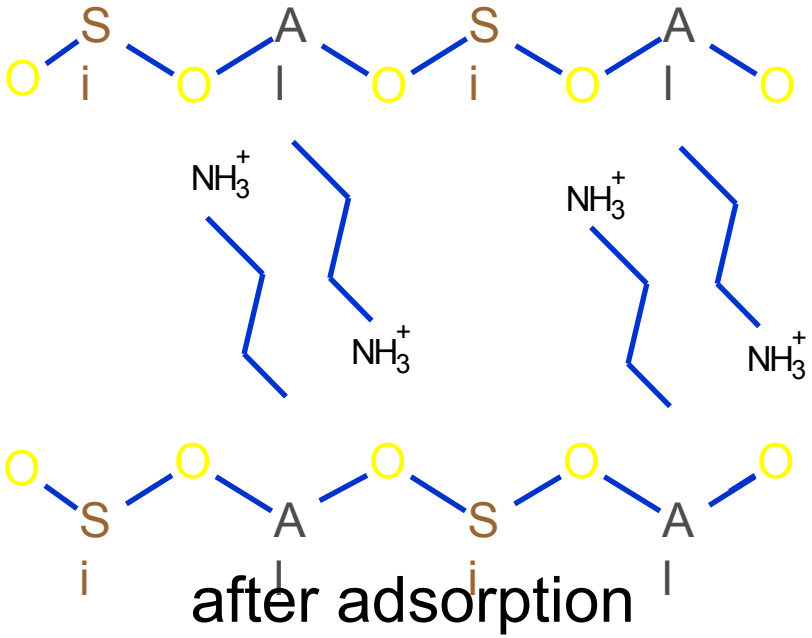
Anger, Brauwelt int. 1996

Bentonite

- Aluminum silicate
- High swelling power → beer loss
- Difficulties with overdosing and prolonged contact time → to strong decrease of high molecular nitrogen substances accompanied with deterioration of foam stability
- Combined application with PVPP is also possible

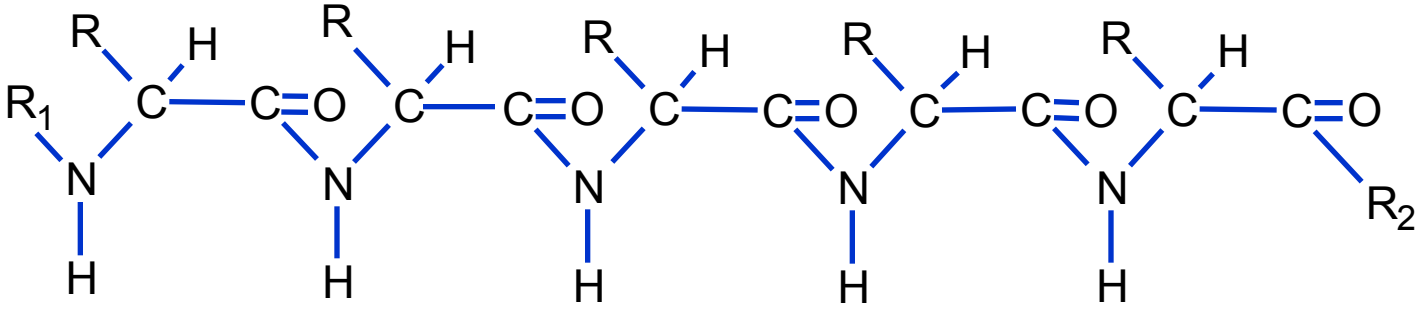
BENTONITE





Cations are exchanged

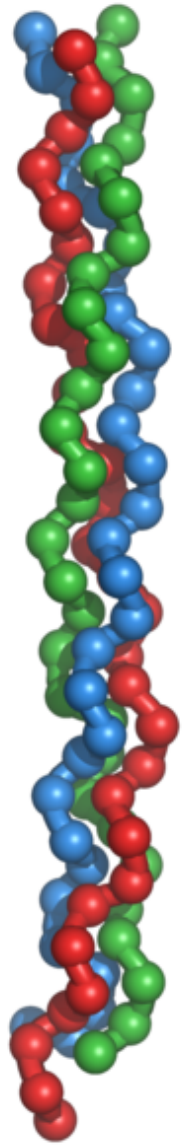
Protein structure



Bentonite stabilized Beers

Bentonite [g/hl]	Proantho. [ppm]	Catechins [ppm]	MgSO4- N [ppm]	Warm days 60°C [EBC]	Foam R&C [sec]	Colour [EBC]
0	4,5	7,1	169	0,4	127	9,7
50	4,0	6,7	136	1,7	123	8,8
150	3,9	6,5	95	5,3	121	6,8

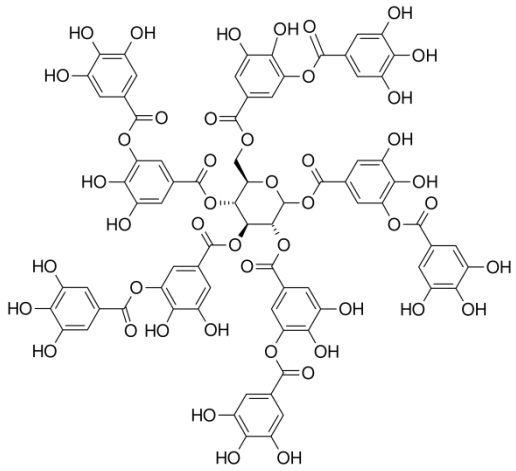
Stabilization by Precipitation: Isinglass



- Effective beer clarification aid. The purified form is produced from the air bladder of the sturgeon and certain other fishes. It consists of 70 % of the protein collagen and is dosed at the end of fermentation. Since the molecular structure of collagen consists of positive and negative charged areas it is able to bind proteins and yeast cells (negatively charged cell wall)
- Possible negative consumer perception because fish products are known to be one of the major food allergens. Although scientific trials indicate that there is no evidence that isinglass could cause allergenic reactions in people who are allergic to fish a small significant sector of consumers might choose not to drink the beer

Tannic Acid

- Natural gallotannins extracted from Chinese gall nuts or Sumac leaves
- Has many hydroxyl groups that attract nucleophylic SH- and NH- groups of haze active proteins in a similar manner as polyphenols to beer proteins during maturation
- Very efficient stabilizer, but produces voluminous precipitates → beer loss, centrifugation necessary
- 5 – 8 g/hl dosed to cold maturation
- Has been found to decrease concentration of the foaming polypeptides in some cases
- Not allowed in some countries (must be indicated on the label in others)



Source: Coors, J. H., (1983) The Practical Brewer: A Manual for the Brewing Industry

Tannins

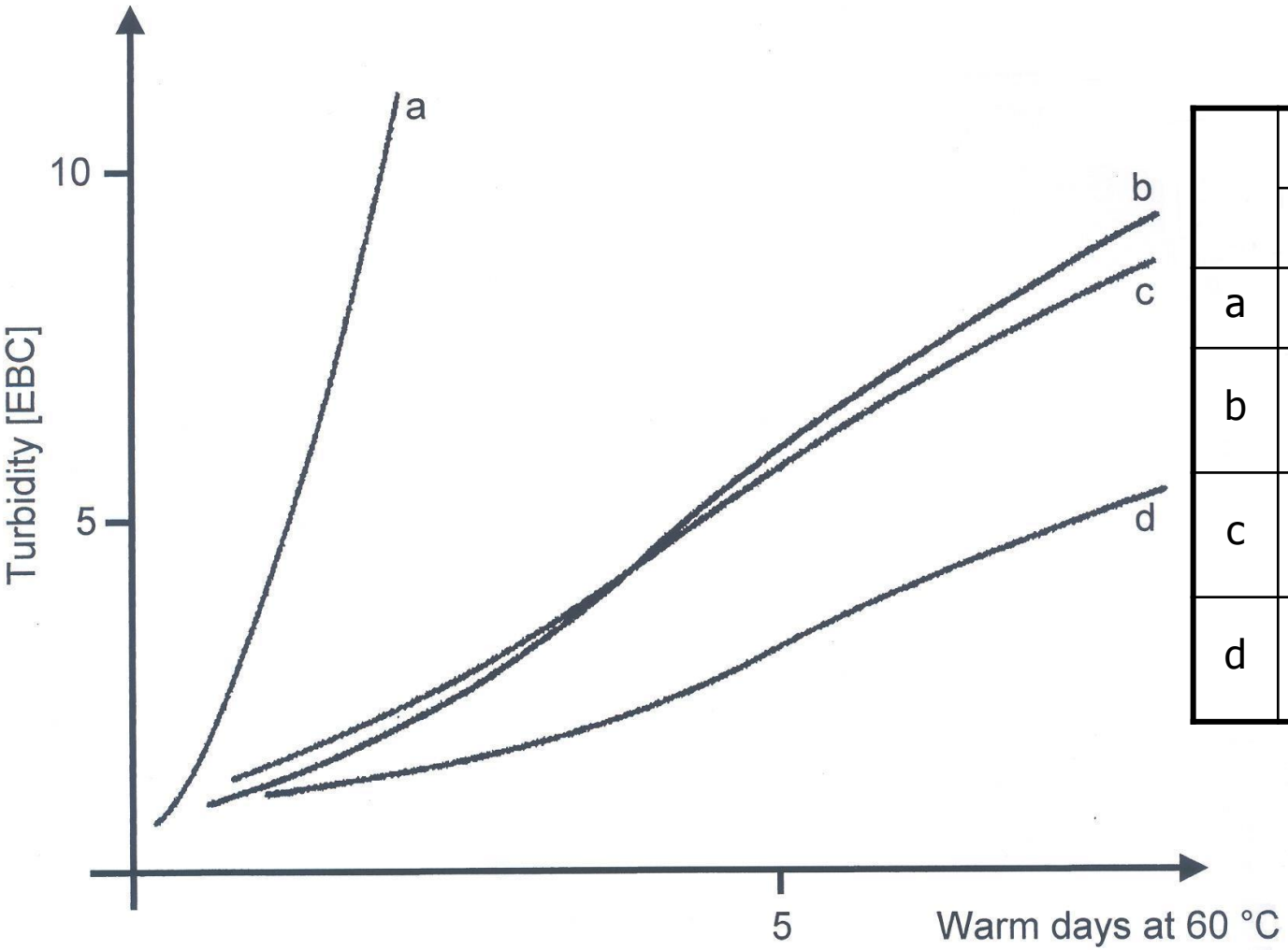
Tannin [g/hl]	Mg-SO_4 – N [ppm]	Anthocyan. [ppm]	Warm days 60 °C [EBC]	Foam R&C [sec]
0	148	43	2,4	117
4	127	35	4,3	118
4+	138	24	>16	118
8	119	36	8,4	117
8+	126	25	>16	116
+ : plus 50g PVPP/hl				

Anger, Brauwelt int. 1996

Proteolytic Enzymes

- Usually Papain produced from the latex of *Carica papaya*
- Hydrolyses proteins
- 2 to 6 ml/hl to rough or bright beer
- Does not differentiate between haze active and non haze active proteins → foam stability is influenced negatively
- Survives normal pasteurisation (< 20 PU's) → continues in bright beer and effects foam negatively
- ADVANTAGE: Cheap
- DISADVANTAGE: Influences foam stability

Papain



	Papain	PVPP
	[2g/hl]	[g/hl]
a	-	0
b	Transfer	0
c	Filtered beer	0
d	Transfer	30

Prolin specific Enzymes

- Specific enzymes attack proteins at prolin sites
- Protein fragments become smaller and therefore better soluble
- Foam active proteins are known to be not rich in prolin, so effects on foam stability are lower then with unspecific enzymes
- Trub active proteins are known to be rich in prolin having lots of sites to be attacked by this enzyme
- The dosage rate is 2 ml/hl and can be added in-line in the fermentation vessel or to the wort before pitching.
- Studies have shown that PSEP can produce a stabilisation comparable with PVPP / Silica Gel.

Enzymatic Stabilisation: Brewers Clarex TM

Advantages (according to the producer)

- higher temperatures during maturation possible
- low investment and energy costs
- No disposal waste
- Can be easily integrated with DE-free filtration technology
- Small liquid dosage has a very low risk of O_2 ingress

Disadvantage

- possibly high 90° turbidity values ("invisible haze")

Sources: DSM Food Specialties / Bamforth, C., (1999), Beer Haze. ASBC Journal