

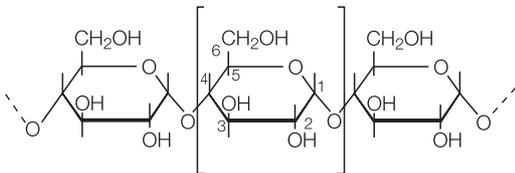
Table of Contents

Cationization of Polymers

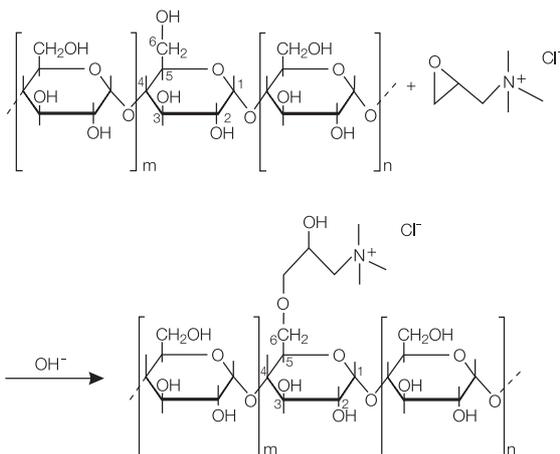
1	Concept, Definitions, Relationships	3
2	Wet Process for Starch Cationization	5
3	Dry Process for Starch Cationization	9
4	Various Cationic Polymers	11
5	Uses for Cationic Polymers	11

1 Concept, Definitions, Relationships

The most important chemical building block of the polysaccharides (e.g. starch, cellulose) is the anhydroglucose unit (AGU).



This unit has 3 OH functions available for etherification with QUAB epoxide. Under suitable reaction conditions, all OH functions can be etherified. For clarity, only the reaction at the C6 position is shown below.



1.1 Degree of Substitution (DS) and Yield

Cationization is measured by the **"degree of substitution" (DS)**. The degree of substitution indicates the average number of hydroxyl groups on each anhydroglucose unit (AGU, $M = 162.15$ g/mole) which are derivatized by substituent groups (QUAB, $M = 151.64$ g/mole). In theory, the maximum obtainable value for starch is 3. The above graphic formula shows the degree of substitution to be $1/(m + n + 1)$.

The degree of substitution is expressed as moles of reagent per anhydroglucose unit:

$$DS = \frac{n_{\text{Quab}}}{n_{\text{AGU}}}$$

When determining the actually obtained ("practical") degree of substitution ($DS_{\text{pract.}}$), only the polymer bound portion is considered. This portion of cationically bound nitrogen ($\%N_{\text{cation.}}$) is measured by Kjeldahl analysis. The calculation of $DS_{\text{pract.}}$ is according to the following formula:

$$DS_{\text{pract.}} = \frac{\%N_{\text{cation.}} \cdot 162.15}{1401 - (\%N_{\text{cation.}} \cdot 151.64)}$$

In starch cationization, practical degrees of substitution of 0.50 and higher can be obtained. Depending on type and origin, biopolymers contain greater or smaller quantities of protein nitrogen. Under alkaline conditions, this protein nitrogen is partially soluble in the reaction medium and is separated when the polymer is washed ($\%N_{\text{soluble}}$). To determine the yield correctly, the percentage of protein nitrogen which is insoluble under the cationization conditions ($\%N_{\text{insol.}}$) must be deducted from the nitrogen content determined after washing ($\%N_{\text{washed}}$). Without this correction yield values would be overstated. Including this correction, the cationically bound nitrogen content ($\%N_{\text{cation.}}$) is:

$$\%N_{\text{cation.}} = \%N_{\text{washed}} - \%N_{\text{insol.}}$$

The yield (reaction efficiency) of the cationization reaction is calculated from the actually achieved degree of substitution ($DS_{\text{pract.}}$) and the theoretically possible degree of substitution ($DS_{\text{theo.}}$) according to following formula:

$$\text{yield (\%)} = \frac{DS_{\text{pract.}}}{DS_{\text{theo.}}} \cdot 100$$

The theoretical degree of substitution ($DS_{\text{theo.}}$) is obtained assuming that the total amount of added reagent (epoxide and chlorohydrin) reacts completely with the polymer; i.e. $DS_{\text{theo.}} = n_{\text{QUAB}}/n_{\text{AGU}}$. This corresponds to a quantitative yield of 100%.

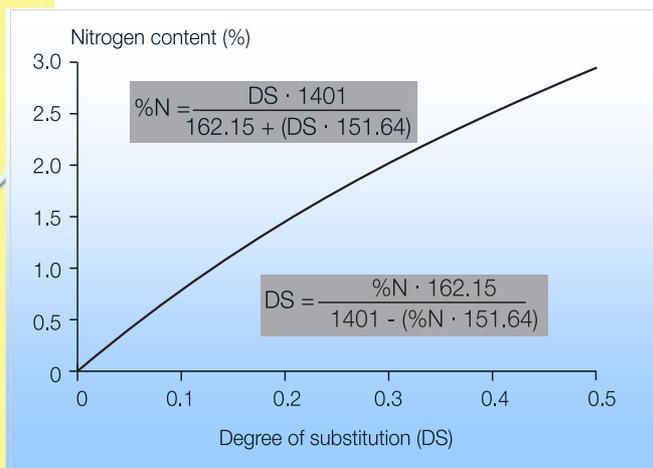
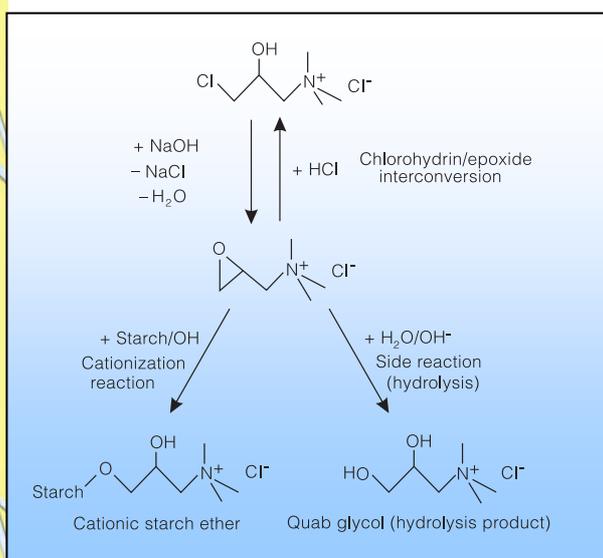


Fig. 1: Dependence of the degree of substitution (DS) on nitrogen content

Yields based on the quotient of the bound (%N_{cation}) and the theoretically expected nitrogen content (%N_{theo.}) give values which deviate from this method because the relation between degree of substitution and nitrogen content is nonlinear (see Fig. 1).

1.2 Cationization of Starch and Hydrolysis of QUAB

The following reaction scheme illustrates the principle of starch cationization as well as the most significant side reaction, the glycol formation.



The "active" reagent for the starch cationization is always the epoxide. This epoxide is either used directly or produced *in situ* from the chlorohydrin by adding a stoichiometric quantity of alkali. Under alkaline catalysis, the epoxide reacts primarily with the starch and forms a cationic starch ether (main reaction). To a lesser degree, however, the epoxide is also hydrolyzed with water to form the QUAB glycol (side reaction).

The extent of the main and side reaction is primarily a function of pH and water concentration. The ratio of the reaction rates between main and side reaction determines the attainable cationization yield. The larger the ratio, the higher the yield. In a process optimization this ratio must be maximized by suitable variation of pH and water concentration. Varying the reaction temperature does not significantly increase the yield because the main and side reaction have similar activation energies. If the temperature is increased, both reactions are accelerated to nearly the same extent. As a result, the ratio between main and side reaction remains basically the same at different temperatures.

The following processes are used for the production of cationic starch ethers and other polysaccharide ethers:

- Wet process (dispersion or slurry process)
- Dry process (semi-dry, dry-heat and Powdercat® process)
- Extrusion process
- Drum drying process

The first two methods will be discussed further in the following chapters since they have the greatest significance for the present market. The last two methods are of secondary importance.

2 Wet Process for Starch Cationization

Conversion of Starch with QUAB in Aqueous Suspensions

Cationic starches are produced in large quantities by a wet process, i.e. through reaction in aqueous starch suspensions. Fig. 2 schematically shows the individual process steps.

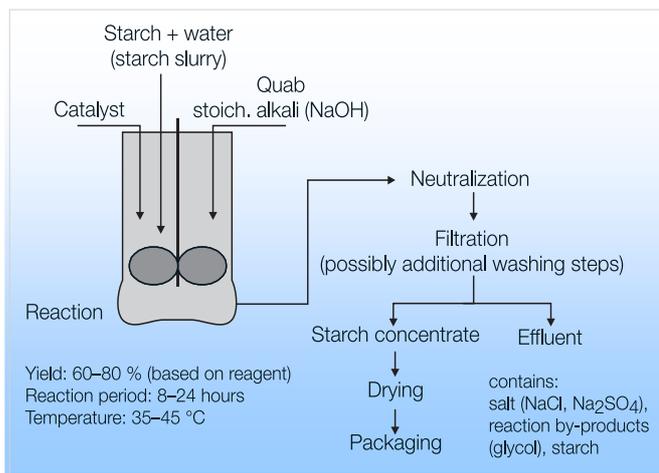


Fig. 2:
Schematic representation of the wet process

General Procedure Using QUAB 188

Depending on the desired degree of substitution, a starch suspension is mixed with the appropriate quantities of QUAB 188 and alkali. The alkali is used for conversion to the epoxide and catalysis of the cationization reaction. This mixture is then heated to 35-45°C and stirred for 8-24 hours. After neutralizing, filtering and washing, the starch is dried and packaged.

- **Laboratory formulation for wet cationization of various starch types with $DS_{\text{pract.}} = 0.035$ (0.29 %N_{cation}.)**

Water, QUAB 188 and the stoichiometric quantity of NaOH are introduced into a three-necked flask equipped with a stirrer. The starch is then added and the required quantity of catalytic NaOH is injected dropwise over a period of 30 minutes while stirring vigorously. After the addition has been completed, the reaction mixture is heated to 40 °C and stirred at this temperature for 24 hours. Diluted acid (e.g. 10 % HCl) is then used to adjust the pH to 5-7. The slurry is filtered and the obtained filter cake is washed with water and dried.

Yield Optimization

A frequently asked question is how to optimize the yield (reaction efficiency) of wet cationization. One option is to **increase the starch concentration** or to **decrease the water concentration** in the slurry, since less QUAB glycol is formed at a lower water concentration.

Water concentration, however, can be minimized only to a certain limit. Due to chemistry a minimum quantity of water or moisture in the starch is always needed for the cationization reaction. This fact has led to the development and use of „dry“ processes (see chapter 3). In a wet process, minimization of the water concentration is subject to technical constraints. If the water content gets too low, the slurry can no longer be stirred or pumped efficiently.

Concentration of starting mixture: 40% starch (d.s.b.*) in total mixture

Starch type	Potato	Corn	Wheat	Tapioca
Moisture	18 %	12 %	12 %	16 %
Assumed yield	80 %	70 %	60 %	70 %
Starch (air-dry)	200 g	200 g	200 g	200 g
QUAB 188 (69 %)	12.1 g	14.8 g	17.3 g	14.1 g
Stoichiometric NaOH (30 % solution)	5.9 g	7.2 g	8.4 g	6.9 g
Catalytic NaOH (10 % solution)	24.6 g	26.4 g	17.6 g	33.6 g
Additional water	167.4 g	191.6 g	196.7 g	165.4 g
Total quantity	410 g	440 g	440 g	420 g

* Dry substance basis.

The following figure schematically shows the influence of starch concentration on yield:

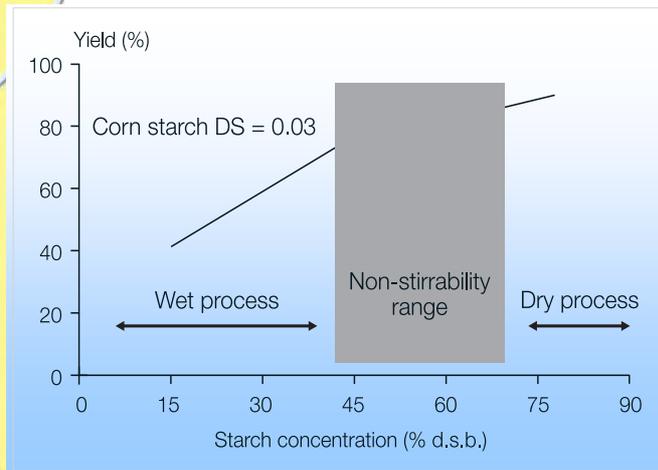


Fig. 3:
Influence of starch concentration on reaction yield

Reaction Time and Temperature

In general, higher reaction temperatures increase the reaction rate and consequently decrease reaction time. The maximum temperature achieved in practice, however, is a function of the starch swelling behavior and the alkalinity of the mixture (pH). It is therefore necessary to determine the optimum temperature at which the swelling of the starch is sufficiently low that the reaction mixture can still be stirred and filtered.

Salt Addition

Electrolytes (e.g. sodium chloride, sodium sulfate) can be added to prevent undesirable swelling of the starch. Sodium chloride, which is formed during the activation of QUAB 188 with NaOH, already reduces swelling. Additional sodium chloride is not recommended because this leads to a decrease in yield and an increase in reaction time. Excessive use of additional salt can also cause effluent problems.

Slurry Dilution

Some cationization processes use a starch slurry directly from native starch production. In this case a minimum water concentration is given and each subsequent addition of reagents causes further dilution of the starch slurry. In order to avoid undesirable losses in reaction efficiency and production capacity it is advantageous to prevent further dilution.

This can be achieved, for example, by the following measures:

- Preactivating QUAB 188 (outside the reaction mixture)
- Increasing the alkali concentration required for stoichiometric activation of QUAB 188
- Using QUAB 188 of higher concentration (69 % instead of 65 %)
- Using the epoxide (QUAB 151) instead of the chlorohydrin (QUAB 188)

Use of QUAB 151

Using QUAB 151 instead of QUAB 188 in the wet process will improve yields and reaction rates which in turn leads to higher capacity and shorter reaction times.

Fig. 4 shows representative results of laboratory tests for the cationization of potato and corn starch using QUAB 188 and QUAB 151. The use of QUAB 151 results in an increased final yield, which is clearly higher for potato starch compared to corn starch.

QUAB 151 has a twofold effect of **increasing the slurry concentration of the starting mixture** and thereby **maximizing the yield**:

1. Increasing the slurry concentration by avoiding the stoichiometric addition of alkali needed for chlorohydrin activation.
When QUAB 188 is used, a dilution of the starch slurry is unavoidable because the formation of epoxide requires the addition of aqueous alkali. The use of QUAB 151 eliminates this stoichiometric activation of chlorohydrin and therefore reduces the amount of water added to the slurry.
2. Increasing the slurry concentration through higher active matter concentration of QUAB 151. An additional advantage of using QUAB 151 is its higher active matter which reaches up to 75 % (total active matter, calculated as epoxide). As a result, less water is introduced into the slurry than is the case with the more diluted QUAB 188. Due to the difference in molecular weight the active matter content of QUAB 188 (69 %), calculated as epoxide, is only approximately 56 % and for QUAB 188 (65 %) approximately 52 % respectively.

The following calculation illustrates the advantage of using QUAB 15 1:

Assuming a slurry of corn starch has a concentration of 43 % (d.s.b.). A cationic corn starch with $DS_{\text{pract.}}$ 0.03 and 0.05 is to be produced. The attainable yield is assumed to be at 70 %. The concentration of the sodium hydroxide solution used for stoichiometric activation of chlorohydrin (when using QUAB 188) and catalysis of the cationization reaction is 5 %. A total amount of 1.5 % NaOH in relation to dry starch is added. The following table shows the final starch concentration when QUAB 188 (65 % and 69 %) and QUAB 151 are used for both degrees of substitution. The percentage by which **production capacity can be increased with QUAB 151** was also calculated.

Practical DS		QUAB 188 (65 %)	QUAB 188 (69 %)	QUAB 151 (74 %)
0.03	Starch concentration in total mixture:	34.3 %	34.3 %	37.1 %
	% higher production capacity when using QUAB 151	8.2 %	8.0 %	-
0.05	Starch concentration in total mixture:	32.2 %	32.3 %	36.5 %
	% higher production capacity when using QUAB 151	13.4 %	13.2 %	-

The calculation clearly shows that the capacity increase obtained by using QUAB 151 instead of QUAB 188 is a function of the degree of substitution. The scheme does not take into consideration that final yields can also be higher by about 5 % with QUAB 151 (see Fig. 4).

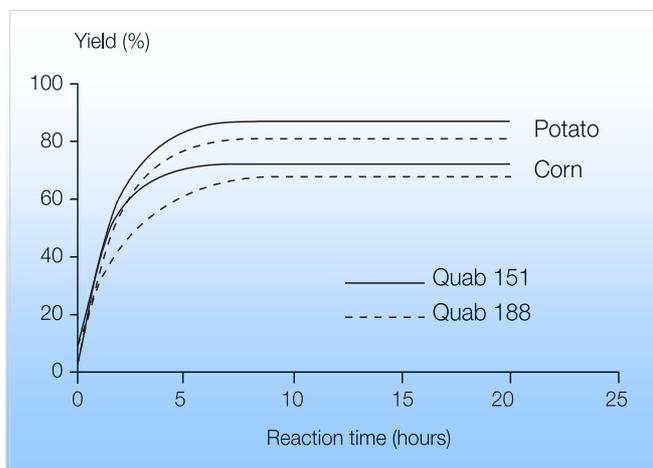


Fig. 4.- Yield Comparison for QUAB 188 and QUAB 151 (wet process)

A further advantage of QUAB 151 compared to QUAB 188 is the **better utilization of the available storage volume**. If the active matter concentration in QUAB 188 is calculated as epoxide, it follows that 1 liter of QUAB 188 (65 % chlorohydrin) corresponds to a volume of 0.74 liter of QUAB 151 (73 % epoxide) or 1 kg of QUAB 188 corresponds to a quantity of 0.71 kg of QUAB 151.

This means in practice, for example, that a 20 m³ tank filled with QUAB 151 contains approximately 16.5 tons while the same tank filled with QUAB 188 contains approximately 12.2 tons of active matter (calculated as epoxide).

During conversion of chlorohydrin to epoxide, stoichiometric quantities of sodium chloride are formed. As a result, the quantity of salt to the effluent increases. With the use of QUAB 151, no sodium chloride is formed. **QUAB 151** thus substantially contributes to the **on-site decrease of the total salt burden**.

In summary, the following can be stated:

Using QUAB 151 (epoxide) in wet cationization offers the following advantages with respect to QUAB 188 (chlorohydrin):

- Higher yields
- Higher production capacity
- Lower salt burden
- Lower NaOH consumption (only for reaction catalysis)
- Higher active matter content (calculated as epoxide) per available storage volume
- More economical starch cationization

Cationization of Starch in Organic Solvents

One variant of the wet process is the cationization of starches in organic solvents. Here, the side reaction to form QUAB glycol is clearly repressed. Moreover, many organic solvents prevent starch from swelling. This allows higher reaction temperatures and leads to shorter reaction times compared to cationizations in water. The use of salts as swelling inhibitors is also avoided. A major disadvantage is that organic solvents present a fire and explosion hazard. The special requirements involved for fire protection and occupational safety and health limit the use of this type of cationization technology. Furthermore, there are additional costs for solvent recycling and disposal.

▪ **A laboratory guide-formulation for a $DS_{\text{theo.}} = 0.06$ is as follows:**

224.0 g	isopropanol
39.0 g	water
116.0 g	wheat starch (10.8 % moisture)
10.4 g	QUAB 188 (69 % active matter)
3.2 g	NaOH (of which 1.53 g are the stoichiometric and 1.67 g are the catalytic quantity)

The mixture is stirred for 4 hours at 65 °C. When the reaction is complete, hydrochloric acid is used to neutralize to a pH of 5. The starch is filtered, washed with an isopropanol-water mixture and dried to a residual moisture content of approximately 6 %.

pH-value	5-6
settleable substances	< 0.1 ml/l
COD (Standard methods)	9300 mg O ₂ /l
BOD ₅	approx. 3600 mg O ₂ /l*
Organic carbon, TOC (Beckmann analyzer)	4660 mg/l
Fish test:	Lebistes survive 48 h at a minimum dilution of 1 : 6.7
Damage units in accordance with the German Regulation on Effluent Release	20.6/100 m ³ per year

Process Effluents with Wet Cationization Using QUAB

Examination of effluents has shown that filtrates of the cationization reaction have a relatively minor impact on the environment. Salt contents are not taken into account in this assessment. For example, the following effluent-related parameters were determined for the filtrate of a cationic potato starch prepared in an aqueous suspension (theoretical degree of substitution 0.06):

**Extrapolated based on R. Wagner, "Vom Wasser" 42 (1974), 272-305*

Control and monitoring of the total impact of process effluents continues to gain in importance due to prevailing local and regulatory conditions. It is therefore understandable that users show a great interest in solving their waste water problems. The dry process - particularly when using QUAB 151 - can significantly contribute to reducing environmental impact.

3 Dry Process for Starch Cationization

Low to Medium Cationic Starches (DS = 0.01-0.07)

It has been shown that raising the starch concentration (decreasing the water content) significantly increases the yield of the cationization reaction (see Fig. 3). This fact has led to the development of different dry cationization processes. The dry process developed by Degussa is known as the "**Powdercat® Process**" (PC process¹). The flow chart in Fig. 5 shows the different process steps.

In a mixer, starch is vigorously mixed with the **Powdercat Activator**² and **Powdercat QUAB (epoxide)**. The mixture is then transported to suitable storage containers (silos) where the cationization reaction takes place. After the reaction is complete, the starch can be further treated and its properties modified by adding additional substances (e.g. neutralization agents).

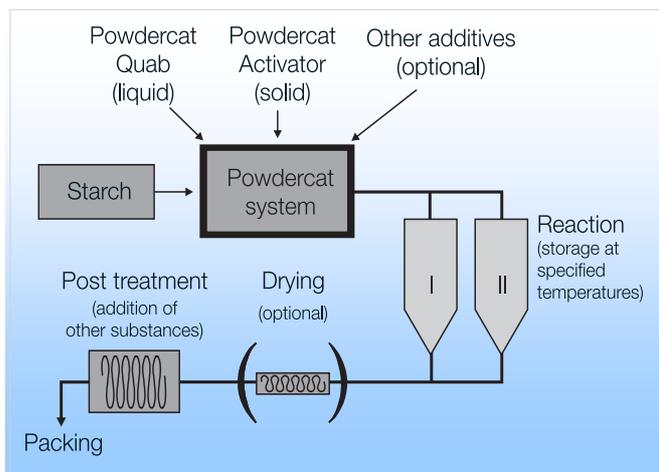


Fig. 5.
Schematic representation of the **Powdercat** process

Highly Cationic Starches (DS > 0.07)

The paper and board industry increasingly demands highly cationic starches with a DS > 0.07. In response to this demand, Degussa has developed a new technology for manufacturing these starches seeing that existing methods do not produce satisfactory results. The wet process is excluded for chemical-technical reasons because cationic starch becomes increasingly cold water soluble above a DS of 0.07; i.e. viscosity of the resulting starch solution increases significantly. In practice, the starch slurry becomes so highly viscous that stirring is impossible or possible only at great energy input. In addition, a high fraction of soluble starch components are lost with the wash water. This is economically and ecologically detrimental. The starch losses reduce the product quantity manufactured per batch and increase the starch burden in the effluent. Here, dry cationization proves to be the only technically successful alternative. Degrees of substitution of 0.5 and higher may be obtained with this technology. Compared to the wet process, dry processes can achieve an approximately 10-fold increase in DS.

The advantages of dry cationization are briefly summarized as follows:

- Higher yields (even with "difficult" starches such as wheat starch)
- No waste water
- Minimum water usage
- Low production costs (compared to the wet process)
- High flexibility (many options for modifying the end product)
- Relatively low investment costs
- Little floor space required
- Degrees of substitution up to approximately 0.5 are possible (compared to the wet process with DS up to approximately 0.07)

1) The PC process is discussed in detail in *Starch/Stärke*, Issued 2/1992, in an article entitled "Production of Cationic Starch Ethers Using an Improved Dry Process." This article is available as a separate reprint.

2) See also "Powdercat Activators for Dry Processes."

Powdercat® Activators for Dry Process

Successful cationization with Powdercat QUAB is only possible in the presence of catalytic quantities of alkali. In practice sodium hydroxide and calcium hydroxide are primarily used for this purpose. Both compounds are relatively inexpensive and easy to handle, but their exclusive use can lead to specific drawbacks. Special attention is necessary with the dry process because here the properties of the final product can be influenced more specifically. To meet market requirements for different property profiles of cationic starches, Degussa has developed special activators. These make it possible to adjust or tailor starch properties. The products are sold under the brand name Powdercat Activator (PC Activator) together with Powdercat QUAB (Epoxide). The Activators are powderous products based on alkaline substances.

Quality parameters of cationic starches that can be positively influenced by the use of PC Activators are:

- High degree of whiteness
- DS up to 0.5
- In many areas adjustable paste viscosity (from low to very high)
- Low slurry viscosity
- High yields
- Good viscosity stability (even with elevated storage temperatures)
- Adjustable flowability
- Low tendency for dust formation

- Good application properties in papermaking (e.g. dry strength, dewatering, retention and flocculation)
- Neutral odor
- Good miscibility in water (hydrophilic starches)
- Easy discharge of silos and big bags

General Procedure for Producing Powdercat® Starches

Native starch and Powdercat Activator are homogeneously mixed in a laboratory mixer. Powdercat QUAB (epoxide) is then sprayed together with the required amount of water onto the mixture and homogenized for an additional 5-10 minutes. The resulting mixture is filled into suitable storage containers and stored at room temperature for 3-7 days. After neutralizing the yield of the cationization reaction is determined based on Kjeldahl nitrogen analysis (see Chapter 1.1 for calculation formulas).

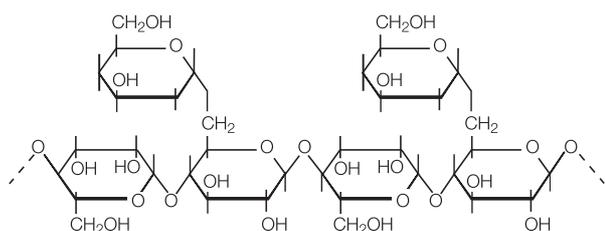
Laboratory formulation for dry cationization of various starch types with $DS_{\text{pract.}} = 0.05$ and 0.18

Starch type	Potato	Tapioca	Corn	Wheat	Potato
Moisture content	18%	12%	12%	12%	18%
Starch	1000 g	1000 g	1000 g	1000 g	1000 g
Powdercat Activator	8.2 g	11.4 g	14.1 g	11.4 g	20.5 g
Powdercat QUAB (epoxide) (73 % active matter)	58.4 g	62.5 g	62.6 g	62.6 g	222.5 g
Water	24.3 g	70.9 g	70.9 g	70.9 g	54.1 g
$DS_{\text{pract.}}$	0.05	0.05	0.05	0.05	0.18
$\%N_{\text{cation.}}$	0.41	0.41	0.41	0.41	1.31
Yield	90%	90%	90%	90%	85%

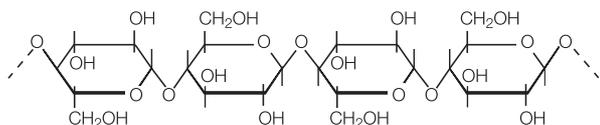
4 Various Cationic Polymers

QUAB can be used to cationize not only starch but also a variety of other natural polymers and their derivatives, such as guar and cellulose.

Non-modified guar gum is already soluble in cold water so that cationization can be performed only in organic solvents (e.g. isopropanol) or by using a dry process.



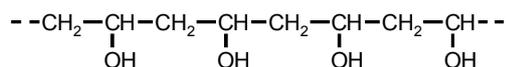
Reaction of cellulose and its derivatives (e.g. hydroxyethylcellulose) with QUAB produces cationic cellulose ethers.



Non-modified cellulose is insoluble in water. Cationization can therefore be performed in water as well. Cellulose derivatives on the other hand are mostly water soluble. Thus, they must be modified in organic solvents or a dry process.

QUAB can be used to cationize not only polysaccharides but other biopolymers as well. Examples are proteins and their hydrolysates, gelatin and chitosan.

QUAB can also be used to convert synthetic polymers. Such cationic polymers are used in many different branches of industry. The following is the most important:



Fraction from the polyvinyl alcohol polymer

5 Uses for Cationic Polymers

■ Paper Industry

In papermaking, large quantities of cationic starch and guar are used as dry strength additives and retention aids. In addition they are used as surface-sizing agents and as coating binders.

■ Cosmetics Industry

The cosmetics industry primarily uses cold water soluble polymers, such as cationically modified guar, cellulose derivatives, protein hydrolysates and chitosan. These are used in hair and skin care products (c.g. conditioners and shampoos).

■ Textile Industry

Guar and starch derivatives are used as warp-sizing aids, in printing pastes and as laundry additives