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3. Acetate Manufacturing, Process and Technology

3.1 Chemistry of Cellulose Acetylation

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Summary: Nowadays Celluloseacetate is mainly produced with the acetic acid process. After an activation with acetic acid and sulfuric acid the acetylation of the cellulose starts by adding acetic anhydride. The temperature and the catalyst concentration play an important role for the reaction. Beneath acetylation also degradation of the cellulose chains occurs. In the first step of the process cellulosetriacetate is formed. In a second step, the hydrolysis, several acetyl groups are removed to achieve an average degree of substitution of 2,5. The water content in this step influences the acetyl distribution.

Keywords: Cellulose; Celluloseacetate; Activation; Acetylation; Degradation; Hydrolysis; Kinetic; Analysis; Acetic acid process; Hemicelulloses

3.1.0 Cellulose Acetate Manufacture – Industrial Processes

Several industrial manufacturing routes were established in the 1920/30's. These differed in the solvent used in acetylation and process conditions and are generally referred to as The Acetic Acid; The Methylene Chloride and The Heterogenerous processes.

Nowadays, by far the biggest amount of commercial cellulose acetate is produced with the "Acetic Acid Process". Although the "Methylene Chloride process" offers some advantages for the acetylation process compared to the "Acetic Acid Process" several operational units using methylene chloride were closed in the past due to the fact that the production costs were high and potential markets disappeared. Several cellulose acetate applications have to respect food laws or pharmacopeia. This chapter focuses mainly on the "Acetic Acid Process". A summary description of the "Methylene Chloride Process" can be found in [1]

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In the Acetic Acid Process, cellulose triacetate initially formed dissolves in acetic acid present in the recipe during the acetylation stage. Within the Acid Process, several variants evolved based on different catalyst (sulfuric acid) levels, acetylation temperatures and cycle times, and can be broadly grouped as below.

1. Low catalyst process, <2% catalyst by weight (based on cellulose) and known as the Drum or Rhodiaceta process.

2. Medium catalyst process, 4-8% catalyst.

3. High catalyst process, 11-15% catalyst, and known as the Dreyfus process.

Sulfuric acid in medium and high catalyst processes acts as a solvating agent, as well as a catalyst and confers enhanced solubility at the cellulose triacetate stage. High catalyst levels, however, promote faster degradation (viscosity loss) of both cellulose and cellulose acetate and hence these processes need to operate at lower acetylation temperatures than the low catalyst process.

The Methylene Chloride Process process developed by Bayer, and known as the Dormagen process, substitutes methylene chloride in the recipe for acetic acid, allowing for 'reflux' cooling to remove the heat of acetylation. Methylene chloride is also a better solvent for cellulose triacetate than acetic acid, which leads to an inherent quality advantage of over other processes and this was widely recognized in the industry. At its peak in the early 60's, the Dormagen process accounted for 15% of world flake production. However, high capital investment and low productivity limited its expansion and also improvements in flake quality from competing Acetic Acid processes eroded its original quality advantage. At one stage, there were some ten Dormagen plants operating around the world and the last of the surviving plants, closed in the UK in 2003.

This Heterogeneous (Non Solvent) Process was based on treating cellulose with acetic anhydride and sulfuric acid catalyst in the presence of a non-solvent for cellulose triacetate. The resultant cellulose triacetate flake was recovered in a fibrous state. The non-solvent was of petroleum ether or toluene type. This process was only used for cellulose triacetate flake and whilst it was first operated around 1911 in the USA, it never accounted for more than 10% of the world triacetate flake or more than 1% of total flake. The last of the Heterogenerous plants closed in the late 1990's. Since the beginning of the 20th century, cellulose acetate has been investigated very intensively, a huge amount of publications and patents can be found in literature. In this chapter mainly the chemical aspects which are relevant for the industrial acetylation of cellulose will be regarded.

3.1.1 Activation of Wood Pulp

Dissolving wood pulp consists mainly of cellulose. The morphology of wood pulp is quite complex. Depending on the wood source, the pulping process and the treatment afterwards, cellulose has a certain ratio of non crystalline and crystalline phases organized in micofibrils. In the crystalline phases, well ordered oriented cellulose fibres form a three dimensional network fixed by inter- and intramolecular hydrogen bonds. The amorphous parts consist of random orientation of cellulose chains. The accessibility for reagents is much better in the amorphous phases. Treating cellulose with water or other swelling agents leads to an increase of accessibility.

Commercial Dissolving wood pulp for industrial acetylation is usually available in sheets packed in bales or rolls. Using the sheets in the process without any pre-treatment makes sufficient triacetylation nearly impossible. A very important step for the whole acetate process is the activation. The main task of the activation is to reach a homogenous accessibility of all cellulose hydroxyl groups for the reagent acetic anhydride. To achieve this, the pulp sheet has to be disintegrated mechanically as well the morphology of the cellulose fibres has to be opened by swelling. The more complete the disintegration and the swelling is makes it easier to achieve complete esterification. Another prerequisite for a complete acetylation is homogenous distribution of the catalyst. Several catalysts are used for acetylation but up to now the usage of sulfuric acid is most common. If sulfuric acid is added to the cellulose/acetic acid system, cellulose sulphate ester is partially formed. Adding sulfuric acid to acetic anhydride leads at lower temperatures to acetylsulfuric acid and then to sulfoacetic acid [2, 3] and then to cellulose sulphate ester.

Perchloric acid is a stronger catalyst than sulfuric acid. Perchloric acid was used in the methylene chloride process in the UK and Germany in conjunction with sulfuric acid to enhance quality levels, particularly of wood pulp grades. In contrast to sulfuric acid, perchloric acid does not combine with the acetic anhydride or the cellulose itself. It is possible to reach almost complete acetylation with a degree of substitution three. Due to the fact that perchloric acid is very corrosive and its salts are explosive, perchloric acid is not preferred in industrial acetylation. Zinc chloride acting as a Lewis acid also catalyzes cellulose acetylation, but requires large quantities. Several other catalysts or catalyst systems for acetylation of cellulose were discovered, but still sulfuric acid is the preferred catalyst for industrial acetylation.

Complete dissolution of the cellulose before acetylation is the best activation, because all hydroxyl groups are easily accessible. Although several solvents and solvent systems for ex. DMAc/LiCl [4], DMSO/PF [5], DMF/Chloral/Pyridine [6] and others were discovered suitable in the past for acetylation , none of them achieved industrial importance, mainly because of economical reasons. For most solvents, only low concentrations of cellulose are dissolvable and/or the recovery of such solvents is quite expensive.
Industrial activations for cellulose acetylation usually consist of these subsequent steps

Mechanical disintegration
Swelling in (aqueous) acetic acid
Sulfuric acid addition

or a combination of these steps. For the pure mechanical disintegration of the pulp, sheet hammer mills can be used. The degree of disintegration is adjustable over a large range. Small Cellulose chips or fluffy material is achievable mainly dependent on the requirements of the subsequent acetylation reactor system. But with the more intensive the treatment in the hammermill, it is more difficult to avoid thermomechanical damage to the pulp itself. This can lead to partial and irreversible deactivation of the pulp resulting in poor quality after acetylation.

The pulp chips or fluff is then mixed with acetic acid and, depending on the process, the catalyst is added at this point or later. To increase the swelling, this step can be performed at higher temperatures or water levels.

A combination of disintegration, swelling, and catalyst distribution is applied in the so called drum process. Here pulp, acetic acid, and sulfuric acid are combined together in the reactor. During the anhydride consumption and the reactor, the pulp disintegrates. Also, higher drum temperatures improve the swelling. Extremely high temperatures in this media should be avoided due to higher degradation of cellulose chains. During the temperature, solid-liquid ratio, water content, and temperature.

Beneath water is a better swelling agent for cellulose than acetic acid it is also possible to make a slurry of pulp and diluted acetic acid in a hydropulper. The water content in the pulp has to be reduced afterwards by displacing the water with acetic acid before acetylation. Otherwise anhydride consumption and heat evolution at the beginning of acetylation would be too high. In general, the efficiency of activation can be increased with time, temperature, solid-liquid ratio, water content and amount of catalyst.

Beside water, other and more effective swelling agents are well known and described for cellulose activation. For example, strong basic agents like NaOH and NH3 are able to swell the cellulose fibres to a large extent. The intermolecular chain distances increase and the hydrogen bonding system is weakened. The extent of such a swelling of the chain to chain distance can be measured for example by X-Ray diffraction. Due to higher accessibility, the reactivity is increased. In highly swollen Cellulose, it is possible to include inert (concerning acetylation) larger molecules or to introduce “spacers” ethylene or propylene oxide by hydroxyalkylation [7]. Both keep the higher reactivity in the cellulose towards acetylation after exchange of the basic swelling agent.

3.1.1.1 Raw Materials for Acetylation

The basic raw materials for the Cellulose acetate production are high-purity dissolving wood pulp, acetic acid, acetic anhydride and sulfuric acid.

One of the important end uses for Cellulose acetate is production of fibres, such as Filter Tow or textile applications. To achieve high quality and desired property demands for spinning, high quality cellulose acetate is necessary. The usage of highly purified pulps for acetate production is recommended. The pulp should have high brightness to reach a white fiber colour, low amount of impurities (resins, waxes, salts etc.), and high alpha cellulose content which are important for low spinnerette plugging and good spinning properties.

Remaining hemicelluloses in wood pulp, which are acetylated as well, have a negative impact on the properties of cellulose acetate. Glucomannans are a contributor to cellulose acetate haze, falseviscosity and poor filtration. The xylans can have negative impact mainly on color [8].
Depending on the type of activation process, some physical properties of the pulp sheet are of importance. Nonhomogeneous formation of the fibres in the pulp sheet, density variations as well as high density can impact activation negatively. The moisture content should be not too low because local overheating can lead to worse activation. To achieve excellent brightness of the cellulose acetate, acetic acid and acetic anhydride should be highly purified concerning impurities.

Commercially available concentrated Sulfuric acid (technical grade) usually fulfils purity requirements. High quality sulfuric acid was used in the methylene chloride process for speciality plastics grades.

3.1.2 Acetylation

3.1.2.1 General Mechanism

Cellulose can be regarded as a polyalcohol with the typical reactions of an alcohol, like etherification and esterification. The polar hydroxyl alcohol groups of cellulose can be substituted by acetyl groups. Esterification is in equilibrium with the reverse reaction, hydrolysis. The course of the reaction is mainly dependent on the water content in the system. Due to the fact that acetylation is usually performed with a slightly excess of anhydride, there is practically no water in the system, no reverse reaction takes place, and almost quantitatively Cellulosetriacetate is the reaction product. The exact mechanism for acetylation is not completely understood. Nevertheless the following equations, describing proton activity of the catalyst, are widely accepted [9]

$$\mathrm{R(OH)_n + nH2SO4 + Ac2O \rightarrow R(OSO2OH) + 2AcOH} \tag{1}$$
$$\mathrm{R(OSO2OH) + Ac2O \leftrightarrow R(OSO2O-) + Ac2O(H+)} \tag{2}$$
$$\mathrm{Ac2O(H+) + R(OH)_n \rightarrow R(OH)_{n-1}OAc + AcOH} \tag{3}$$

Alternatively another mechanism was proposed taking into account that sulfuric acid combines with cellulose to form cellulose sulfate as intermediate.

$$\mathrm{R(OH)_n + nH2SO4 + Ac2O \rightarrow R(OSO2OH) + 2AcOH} \tag{4}$$
$$\mathrm{R(OSO2OH) + Ac2O \leftrightarrow R(OSO2OAc) + AcOH} \tag{5}$$
$$\mathrm{R(OSO2OAc) + R(OH)_n \rightarrow R(OH)_{n-1}OAc + R(OSO2OH)} \tag{6}$$

Because of intramolecular and intermolecular hydrogen bonds, Cellulose is a more or less partially crystalline three dimensional network. Due to this fact, accessibility of cellulose hydroxyl groups for solvents or reagents is strongly limited. To achieve complete esterification, an efficient activation of the cellulose is required. Although several esterfications in dissolved cellulose are reported in literature which would be the best activation concerning an overall accessibility of the hydroxyl groups, they did not reach any industrial importance up to now.

During the acetylation reaction, degradation always occurs because the glycosidic oxygen bond of cellulose is also subject to acidic hydrolysis. For industrial acetylation, it is always a big challenge to reach almost fully substituted cellulose free of particles with a sufficiently high degree of polymerisation.

The general kinetic dependencies of the degree of substitution and the degree of polymerization during the acetylation are well described in literature [10].

3.1.2.2 Industrial Acetylation

Acetylation can be performed continuously or in a batch process. To keep reactor volume under control, continuous processes are usually combined with higher reaction rates compared to the batch processes. For this, a higher catalyst usage (13 – 15%) is required than in a batch process. With the addition of the acetic anhydride the reaction starts.

The reaction of acetic anhydride with the activated cellulose is exothermic. The temperature profile during acetylation has to be kept under control otherwise significant degradation of the cellulose / cellulose acetate occurs. Cooling of the reactor and/or cooling of the acetic acid and/or acetic anhydride is necessary for almost all processes. One of the advantages of the "Methylene Chloride Process" was the evaporation cooling effect of methylene chloride during acetylation. If the acetylation in the acetic acid process is performed under vacuum a comparable effect can be achieved [11].

A big part of the acetylation reaction is heterogeneous until the end of the reaction where the whole reaction mass becomes a viscous liquid. This allows, by direct or indirect viscosity measurement, adjustment of the degree of polymerization at the stopping point. The stopping of acetylation is normally done by adding water or diluted acetic acid, which destroys the excess anhydride. Sulfuric acid is not usually neutralized, only a desired amount in the high catalyst process, because sulfuric acid is also the catalyst for the subsequent hydrolysis. During the stopping step, a part of the bound sulphates at the cellulose acetate are partially removed, depending on the conditions. After the stopping step, the reaction mass contains water and remaining catalyst so the hydrolysis begins.

3.1.3 Hydrolysis

3.1.3.1 General Mechanism

The industrial hydrolysis of cellulosetriacetate is usually an acid catalyzed hydrolysis.
Starting with the protonation of the carbonyl group, the protonated acetyl group underlies a nucleophilic attack by water with a subsequent deprotonation and splitting off of acetic acid.

$$R(OH)_{n-1}OAc + H_2O \xrightarrow{H^+} R(OH)_n + AcOH$$

During hydrolysis, the oxygen bridge of cellulose acetate is attacked leading to degradation. The general kinetic dependencies of the degree of substitution and the degree of polymerization during the hydrolysis are well described in literature. [12]

3.1.3.2 Industrial Hydrolysis

Acetic hydrolysis of cellulose triacetate needs a certain amount of water (usually 5 – 15 %) which is introduced by the stopping step or by separate addition. Lower temperatures, longer hydrolysis times, and higher water content help to prevent degradation.
Normally the hydrolysis step lasts several hours at temperatures between 50 and 80°C. The desired degree of substitution can be achieved by applying kinetic data or by measuring the acetyl value of the acetic dope.

It is also possible to run the hydrolysis without any catalyst at higher temperatures (120°C – 170°C; high temperature hydrolysis). Under these conditions, hemicelluloses acetates are preferably degraded leading to cellulose acetates having no or only a small prehump. Prehumps are aggregates which can be caused by hemicelluloses with certain chain length. Due to several side reactions at high temperatures, the colour of cellulose acetate has to be carefully controlled. Several additives are proposed to reduce this effect. It is reported that with high temperature hydrolysis, it is possible to use wood pulps with a lower alpha cellulose content to reach the same cellulose acetate quality which was made by standard procedures using high grade wood pulp [13].

Water content in hydrolysis affects the distribution of hydroxyl groups. With increasing water content in the hydrolysis, the primary hydroxyl level in the cellulose acetate increases. [14]

When the desired acetyl value of the cellulose acetate is reached, hydrolysis is usually stopped by neutralizing the catalyst with the addition of salts. Sodium, Calcium or Magnesium salts dissolved in water or aqueous acetic acid can be applied. In principal, it is also possible to stop the hydrolysis by precipitation without a prior neutralisation step. In this case, stabilizing Ions should be present or added in the steps afterwards.

To increase the efficiency of the whole process, it is not unusual to concentrate the hydrolysis solution by evaporating a certain amount of acetic acid before precipitation.

3.1.4 Precipitation, washing and drying

Precipitation can be performed differently. It is possible to dilute the hydrolysis solution until the precipitation point is reached. The corresponding acetate is very fluffy. A large amount of impurities can also be removed. If flakes are desired, it is common to press the hydrolysis solution though holes (spinnerets) into water or diluted acetic acid. After a certain time to complete the precipitation (referred to as maturation), the flakes are washed with water and eventually stabilized by addition of additives.

Before drying, dewatering presses are usually applied to reduce the water content. The cellulose acetate has to be dried carefully afterwards to a water content from 1 – 5 % otherwise partial degradation can occur.

Finally, the cellulose acetate product is stored in silos for further use. Dust formation has to be avoided because dusty cellulose acetate has the potential to form explosive mixtures in air. Inerting of silos both at Flake, Filter Tow, and Filament Yarn plants is practiced by some manufacturers.

3.1.5 Quality and Analysis

Depending on the end use of cellulose acetate, different quality aspects are relevant.
Several standard methods for cellulose and cellulose acetate analysis can be found in literature (ASTM D871-96 Annual Book of ASTM Standards, ISO, Zellcheming). The principles of methods coming from these different organizations are very often similar but differing in the experimental procedure. This is also the fact for several self developed methods applied in the cellulose acetate industry. Below the principles are described.

The main properties describing the overall quality of cellulose acetate are:

Degree of Substitution or Acetyl content

The degree of substitution (DS) or acetyl content has an important influence on the solubility of the cellulose acetate in different solvents. The DS can be determined by a complete hydrolysis of the cellulose acetate with sodium hydroxide in presence of a solvent. The excess of sodium hydroxide is back titrated with hydrochloric acid. Acetyl content for both tri and diacetate is also measured by FTIR spectroscopy.

Degree of Polymerisation, Intrinsic Viscosity

The degree of polymerisation (DP) is important for spinning and fibre properties (tenacity). A small amount of cellulose acetate is dissolved in acetone (2 – 5 g/l). The intrinsic viscosity is measured in a capillary viscometer as well the pure solvent. The ratio is called intrinsic viscosity the ratio minus one the specific viscosity. With calibration curves it is possible to calculate the average DP.

Thermal Stability

Thermal stability is very important for several end uses because it is an indicator of the storage capabilities of cellulose acetate.
Cellulose acetate is heated at high temperatures (> 180°C) for a specified time. Changes in colour are quantified visually or by a subsequent colour determination in a solvent. Changes in intrinsic viscosity can be also checked.

Colour

The colour of the cellulose acetate influences the colour of the end product.

Cellulose acetate is dissolved in a solvent and measured with UV-Vis spectrometer or compared visually with colour standard solutions.

Filtration

Depending on raw materials and process conditions, cellulose acetate contains more or less impurities such as unacetylated or partially acetylated fibres. These leads to a reduced filter life time in the filtration process which is usually applied before spinning or other end uses.

A desired amount of cellulose acetate is dissolved in a solvent and filtered through a specified filter media. On one hand it is possible to measure at constant flow the pressure rise per time on the other hand it is possible to measure at constant pressure the filtrated volume per time.

Particles

Alternatively or in addition to the filtration, the particles of dissolved cellulose acetate can be measured. Usually the particles are monitored from about 1 to 100 microns applying a particle counter system. Depending on the amount and the distribution of the particles, behaviour in filtration and to some extent in spinning can be predicted.

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