Macromol. Symp. **2004**, *208,* 61-79

3.2 Industrial Processes

Andreas Hummel

RHODIA Acetow GmbH; Engesserstrasse 8, 79108 Freiburg, Germany
e-mail: andreas.hummel@eu.rhodia.com

General

In this chapter, industrial processes for producing Cellulose Acetate for cigarette filters and textile applications are explained in detail. Due to the limited space in this book, other industrial processes, such as plastic applications or photographic film, are not mentioned.

In the past, there were two basic processes for manufacturing CA: The "Methylene Chloride Process" and "Acetic Acid Process". Since today only the "Acetic Acid Process" is of industrial relevance, the following chapter is related exclusively to it.

A typical Cellulose Acetate production unit consists of the following major sections:

- Chemical section (pretreatment, acetylation and hydrolysis)
- Processing (precipitation, washing, drying)
- Acetic Acid recovery unit
- Acetic Anhydride production

Specific investment for a Cellulose Acetate production unit is relatively high. Therefore it is only economical to build big units. The smallest plants existing today produce 15.000 t of Cellulose Acetate per year. In recent years, worldwide tendency has been for closure of smaller sites, some bigger sites were debottlenecked, and few new plants were built. This concentration on a few big acetate sites can be explained by the globalization. Filter Tow plants are built all over the world in close proximity to cigarette manufacturing sites. The required Cellulose Acetate can be produced anywhere and easily be shipped worldwide.

DOI: 10.1002/masy.200450406

The first processes used to produce Cellulose Acetate were batch mode. This allowed adjusting process conditions to variations of raw material properties or ambient conditions individually for each batch. Batches from acetylation were treated separately from activation/acetylation, precipitation and washing until drying. After analysis of final product quality, individual batches were blended together for further use.

Nowadays variations in quality of raw materials, as well as means for quality control, have improved greatly. Together with in-line analysis and intelligent control strategies, it is now possible to run continuous processes at high quality levels. Continuous processes need fewer workers and are better suited for higher production capacity. Today, continuous processes for both acetylation and hydrolysis account for 15% of world flake production.

Overall mass balance of Acetic Acid

Simply stated, Cellulose Acetate is Cellulose with some acetyl groups. Therefore, the main raw materials needed for a Cellulose Acetate plant are Cellulose (mainly purchased as wood pulp, sometimes as cotton linters) and acetyl (purchased as Acetic Acid or Acetic Anhydride).

Economically, it is not possible to run a Cellulose Acetate plant without integrated Acetic Anhydride production. There would be an excess of Acetic Acid that needed to be sold. The minimum necessary Acetic Anhydride production for a Cellulose Acetate plant is shown in Figure 1. In Figure 2, the acetyl balance for being self sufficient in terms of Acetic Anhydride is shown.

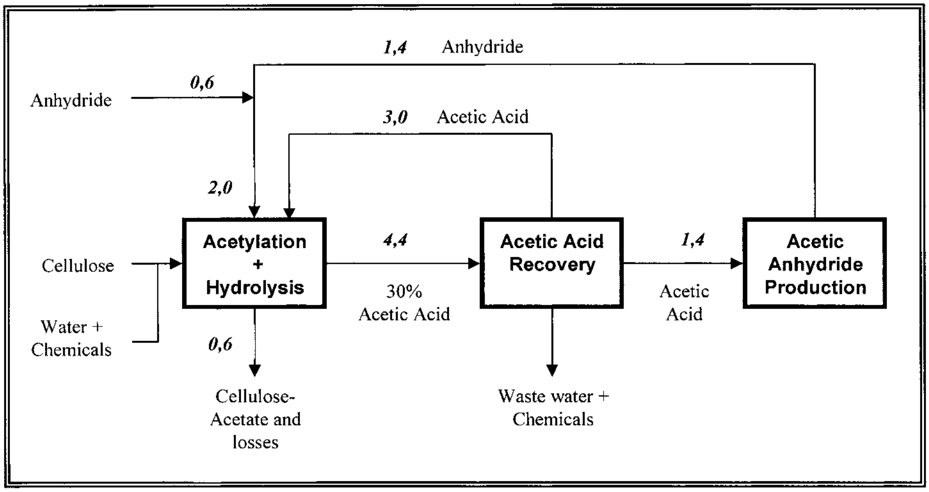

Figure 1: Simplified acetyl balance of a Cellulose Acetate plant with only Acetic Anhydride as source of acetyls. It shows the minimal conversion rate of Acetic Acid to Acetic Anhydride for the given scenario. The units of the figures is ton Acetic Acid per ton of CA.

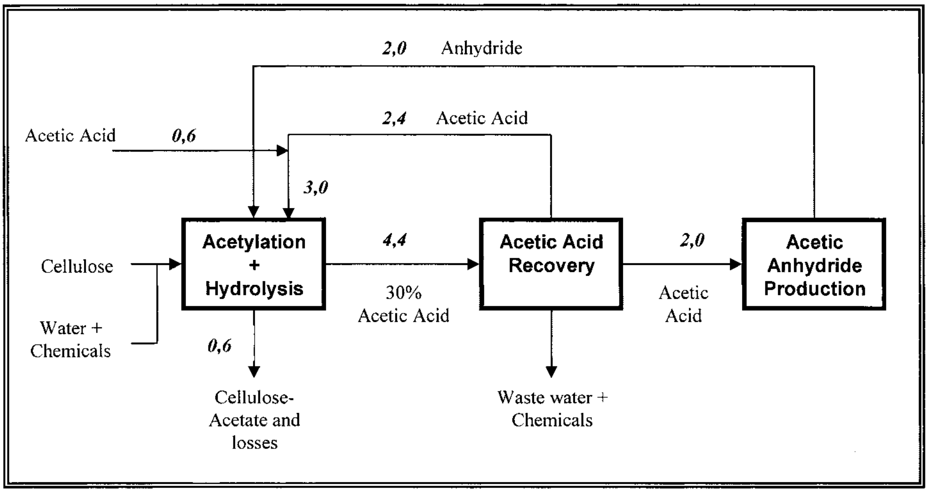

Figure 2: Simplified acetyl balance of a CA plant with Acetic Acid as source of acetyls, self sufficient in Acetic Anhydride. The units of the figures is ton Acetic Acid per ton of CA.

These acetyl balances of the acetate production are simplified. In operating production units, losses are mainly in the washing area, Acetic Acid recovery and mostly in Acetic Anhydride.

Cost structure

Product Cellulose Acetate consists of 45% Cellulose and 55% acetyl groups. As explained above, the main raw materials normally are wood pulp and Acetic Acid. These raw materials are the most important cost factors for Cellulose Acetate. High purity Cellulose has a big impact. Therefore, it is of the utmost importance to optimize the processes to minimize the specific consumption of the raw materials.

Except for the cost for raw materials, which are more or less dependant on the market, energy is the most important cost factor. Direct manufacturing labor is a minor cost factor, since most of the plants worldwide are modern or updated facilities with a high degree of automation.

Materials of construction

Most equipment is in direct contact with acids such as Acetic Acid or Sulphuric Acid. Therefore, the construction material must be corrosion resistant. In the past copper and rubber lined equipment were very common. Today more and more stainless steel is used, but some glass lined equipment is also used. Typical construction materials are 316 stainless steel as standard, 904, hastelloy, and titanium for more severe conditions.

3.2.1 Pretreatment

The chemical and morphological aspects of activation were explained in chapter 3.1.1. In this chapter, industrial processes are described more in detail.

In industrial processes, many different activation methods are used successfully. The activation liquid usually is Acetic Acid, sometimes mixed with Sulphuric Acid. Disintegration of the sheet can be done with dry wood pulp in a hammer mill. The other extreme is to disintegrate the sheets by combining pulp with large volumes of liquid using a hydropulper, but there are many other activation processes somewhere in-between. The main idea is to blend Cellulose with Acetic Acid and Sulfuric Acid to a very homogeneous state.

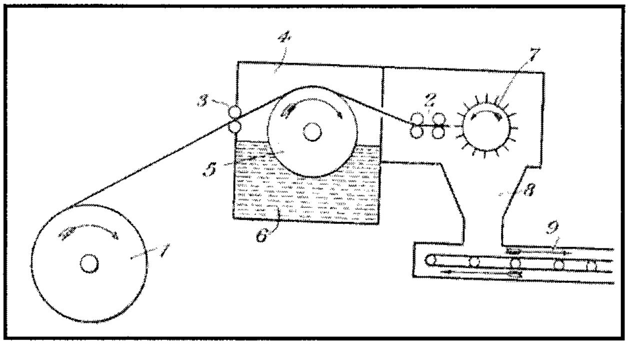

Figure 3 [1] **:**
Activation of cellulose from rolls (1) by soaking it with the activation liquid (6) on a roll (5) before disintegrating it in a hammer mill (7)

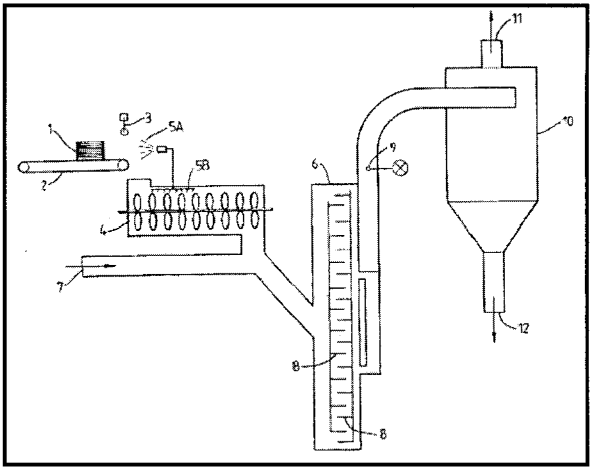

Figure 4 [2]**:**
Activation of Cellulose (1) by wetting it with water (5) before disintegrating it in a shredder (8) and drying by hot air (7) in an Atritor

3.2.2 Acetylation

The chemical aspect of acetylation was detailed in chapter 3.1.2. In this chapter, the industrial process is described more in detail.

Temperature control is a major concern. Two major reactions are exothermic: Water from activation reacts with Acetic Anhydride (H_r = 3300 kJ/kg water) and the acetylation reaction (H_r=1030 kJ/kg Cellulose)[3]. In addition, the dissipated energy from the agitator heats up the reaction mass.

There are different ways to control the reaction temperature:

- Cooling the acetylation mixture (Acetic Anhydride and Acetic Acid), which represents a big portion of the total mass, with a very low solidification temperature.
- Adding frozen Acetic Acid (freezing point 16,75°C), either as Acetic Acid flakes or slurry of Acetic Acid crystals in Acetic Acid /Acetic Anhydride.
- Indirect cooling of the reactor walls and agitator.
- Direct cooling by evaporation of a solvent (Acetic Acid under vacuum or Methylene-Chloride)

Typical acetylation temperatures are

25 - 35°C	activated Cellulose
-20 - 0°C	acetylation mixture (Acetic Acid and Anhydride)
45 - 85°C	reaction temperature at stopping
50 - 75°C	after stopping

Another important parameter is solids concentration during the acetylation reaction. High solids concentration reduces the reactor volume and the amount of Acetic Acid that must be recovered. On the other hand, a lower concentration allows better diffusion of the reagents and acts as an internal cooling by the latent heat of the liquids. Most industrialized acetylation processes use a concentration between 5 and 9 parts liquid per part of bone-dry Cellulose.

The classical acetylation reactor was operated in batch mode. Several different mixers were used successfully, such as horizontal double-Z mixers, plough mixers, or rotating drums. The main requirement for a batch reactor is to avoid dead zones and to allow indirect cooling. The disadvantage of a batch reactor is the small batch size, which is limited mainly by mechanical constraints and reduced cooling capacity.

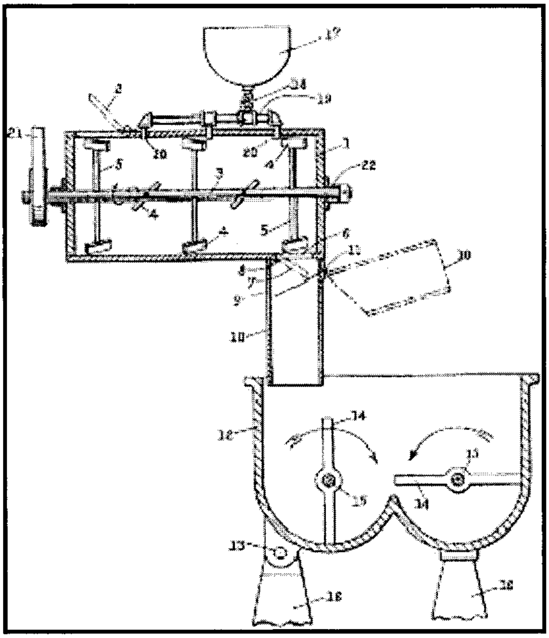

Figure 5 [4]

Activation and Acetylation in horizontal mixers

The shredded Cellulose is added to the mixer (1), activation liquid is added (17,18,19,20) and mixing is performed by the paddle mixer (3, 4, 5).

After activation, pulp falls down to the acetylation reactor (12) with two agitators (14, 15)

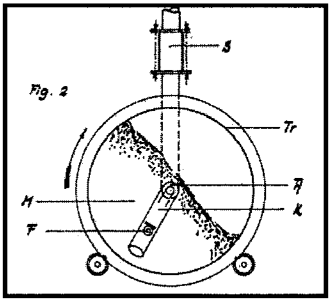

Figure 6: Rotating drum reactor for acetylation [5]
The slowly rotating, partially filled drum (Tr) mixes the reaction mass (M) and allows cooling by a double wall.

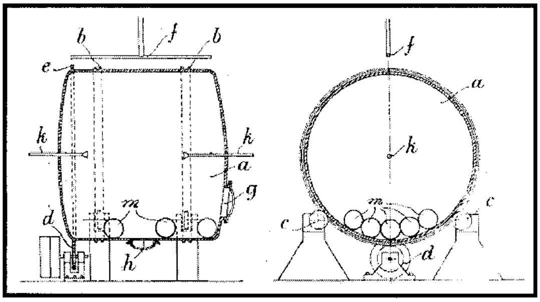

Figure 7: Rotating drum reactor for acetylation [6]
The slowly rotating, partially filled drum (a) mixes the reaction mass by metal balls (m). Indirect cooling is possible by percolation of cooling water on the outer shell (f)

Continuous acetylation reactors are better suited for higher production capacities. Here, it is important to have a good plug flow in order to allow a constant reaction time for all Cellulose fibers. The reaction temperature can be adjusted by indirect cooling or by direct cooling using cold reagents or adding frozen Acetic Acid.

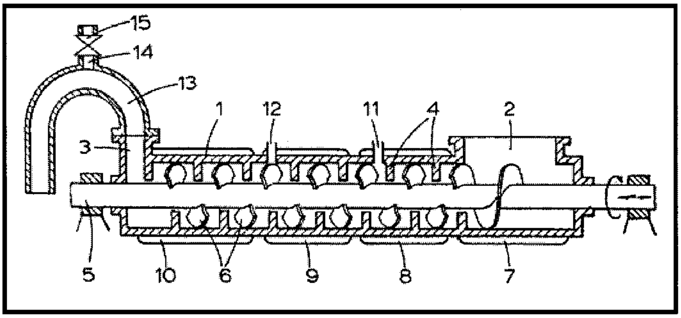

Figure 8: Continuous acetylation reactor [7]
By rotation and horizontal movement of the agitator (5) this reactor has high shear rates and good heat transfer for indirect cooling the reaction (7 – 10).
2: Feed
3: Dope discharge

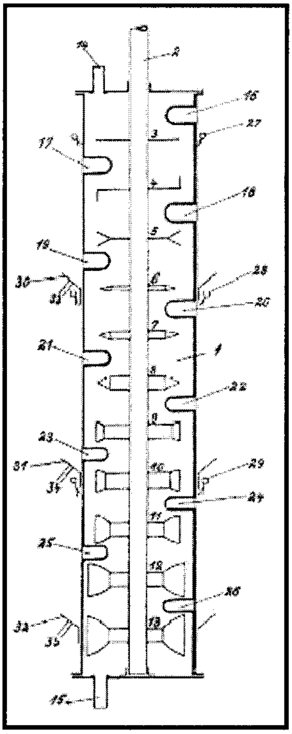

Figure 9: Continuous acetylation reactor [8]
In this reactor the product flows by gravity from top (14) to the bottom (15).

The agitator (2) has different blades (3 – 13), which are adapted to different properties of the reaction mass, starting from fibrous on top, very viscous in the middle, and viscous liquid at the bottom.

Stators (16 – 26) avoid the rotation of the whole mass inside the reactor.
The reactor could be cooled from outside (27, 29)

At the end of the continuous acetylation reaction there may be fibers, which did not completely react. This could be due to insufficient activation of these fibers or because of poor plug flow behavior of the reactor. It is possible to retain these fibers in the reaction zone by a special filter until they react, dissolve and pass the filter [9]. This device can reduce the particles of the final product significantly.

As mentioned above, the "Methylene Chloride process" uses evaporation of a solvent for cooling the reaction mass. This efficient way of cooling can also be applied to the Acetic Acid process[10], but to evaporate a mixture of mainly Acetic Acid and Acetic Anhydride in the reactor, a vacuum must be used.

The purpose of quenching (or stopping) is not to stop the acetylation reaction itself, but to stop the chain degradation at the requested DP (see 3.1.3). This can be achieved by quickly cooling down the reaction mass (addition of cold liquids) and/or by neutralizing the catalyst (Na- or Mg-Acetate solution). Usually the quenching/stopping liquid is a 30 to 60% Acetic Acid solution in water, whose amount is calculated to adjust the water concentration for the subsequent hydrolysis reaction.

Intensive mixing is required to avoid any precipitation of Triacetate, since solids would not react to Diacetate in Hydrolysis any more!

During addition of the dilute acid, the excess of Acetic Anhydride reacts with the water under heat formation. This effect is overcompensated by the latent heat of the cold stopping liquid.

3.2.3 Hydrolysis

The objective of Hydrolysis is reducing the Degree of Substitution (DS) of the Cellulose Acetate from three acetyl groups per Cellulose to a range of 2.4 to 2.5. The chemical background of Hydrolysis was already given in detail in chapter 3.1.3.

The main parameters to control the hydrolysis reaction are water concentration, reaction time, temperature and Sulfuric Acid concentration (catalyst).

The process conditions are more or less the same in most industrial processes, no matter if is a batch or continuous process. Only the so-called “High Temperature Hydrolysis” has completely different process conditions, which will be described later.

- Water concentration: 5 to 15%, adjusted by the amount of water added during the stopping of acetylation reaction.
- Reaction time: between 3 and 10 hours.
- Temperature: between 60 and 80°C.
- Catalyst concentration: 0,1 to 1%, determined by the concentration used in acetylation or increased by adding more Sulphuric Acid.

High Temperature Hydrolysis

A completely different hydrolysis process that is applied industrially is the so-called high temperature hydrolysis [11, 12, 13].

The main difference is that the reaction takes place at a much higher temperature level than standard processes mentioned above. At temperatures of 140 to 150°C, the hydrolysis does not need any catalyst and it reaction time is much shorter (0.5 to 2 h). The disadvantage of this process is increased color of the intermediate product caused by secondary reactions[14]. This color requires special process conditions in precipitation and washing.

The process in more detail: After stopping the acetylation reaction, the catalyst is neutralized completely by adding Magnesium Acetate. By directly adding steam to the dope in the pressure vessel, water concentration and temperature are adjusted. After the necessary hydrolysis time (0.5 to 2 hours) the reaction is slowed down by flash cooling the dope by vacuum. The distillate, Acetic Acid of about 80%, is recovered from the dope.

Industrial equipment

In industrial processes, there is a variety of equipment used for hydrolysis. For batch processes, the standard equipment is an agitated vessel.

For continuous processes, there are patents proposing different reactors that provide more or less plug flow of the viscous dope resulting in a narrow spread of the Degree of Substitution (DS). It could be a cascade of agitated vessels in series, a cascade of towers with special rotating internals[15], or towers filled with static mixers [16].

One example of a continuous industrial application is shown in Figure 10.

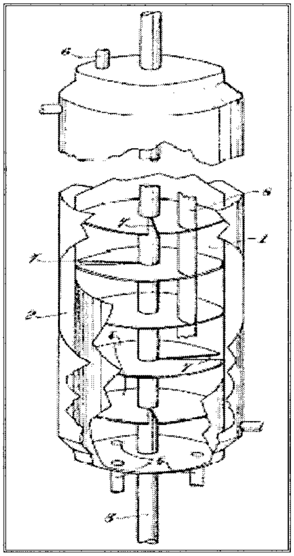

Figure 10: Equipment for continuous hydrolysis of Cellulose Acetate [15].

The acetic dope is fed from the top (6) into a vessel with double jacket
(2) for regulating temperature.
The vessel is divided into compartments (1) by slowly rotating
plates (4)
with a slot (7) for the passage of the dope.
The hydrolyzed dope is discharged at the bottom (5)

Stopping of hydrolysis reaction

After reaching the desired degree of substitution, the hydrolysis reaction must be stopped. This can be done in different ways:

- <u>Precipitation:</u> During precipitation with dilute Acetic Acid, the hydrolysis reaction is slowed down because the temperature is lowered by adding the cold liquid. This method is used if there is no further treatment of the dope after hydrolysis (see also 3.2.4)

- <u>Neutralization:</u> The catalyst (Sulphuric Acid) can be neutralized by adding Ammonia, Sodium-Acetate, or Magnesium-Acetate. This stabilizes the dope for storage or thermal treatment.

- <u>Flash cooling:</u> For the “High Temperature Hydrolysis” process, it is sufficient to reduce the temperature to 50 to 60°C by flash cooling, since no active catalyst is present.

3.2.4 Dope concentration

After hydrolysis, acetic dope has a concentration of Cellulose Acetate of 12 to 18%. The viscosity is comparable to honey. Before precipitation of the Cellulose Acetate, it is possible to recover some of the Acetic Acid, the so-called dope concentration. The recovery cost of Acetic Acid by dope concentration is lower compared to the recovery by Liquid/Liquid-Extraction (see chapter 3.2.7).

One possibility is flash evaporation, as already mentioned in the chapter about "High Temperature Hydrolysis" by Daicel and Celanese. Here the hot Acetic Acid dope is flashed into vacuum and distillate is recovered. This principle of flash evaporation can also be used with standard hydrolysis conditions via direct or indirect heating of the dope before flash evaporation.

A completely different process is dope extraction. In an extraction column, dope is treated by vapor with higher water concentration, extracting Acetic Acid from and adding some water to the dope. The vapor with higher Acetic Acid concentration is purified in a rectification column producing glacial Acetic Acid.

After any dope concentration process, the viscosity of the dope is higher than before. The subsequent precipitation process must be capable of handling the higher viscosities and producing pellets with good extraction and dissolution properties.

3.2.5 Precipitation and Processing

Precipitation

Precipitation processes can be divided in two classes characterized by the bulk density of the resulting acetate particles. Low-density acetate is a fibrous or dusty powder with a bulk density of 200 – 300 kg/m³. High-density acetate has the form of more or less regular pellets of 2 – 5 mm, with a bulk density in the range of 400 to 600 kg/m³. These acetate pellets are much easier to handle, compared to the low-density flakes that can create problems at storage silos and pneumatic conveying. Also, for shipping acetate long distances to the final customer, it is more economical to use pellets with higher bulk density. On the other hand, low-density acetate has advantages in washing, drying and dissolution in acetone due to shorter diffusion length.

There are several patents published for precipitating these different Cellulose Acetate particles. Low density Cellulose Acetate is produced by diluting the polymer solution with water in an agitated device, until the acetate is no longer soluble (see Figure 11). The precipitated Cellulose Acetate is fibrous, porous and has a high surface area.

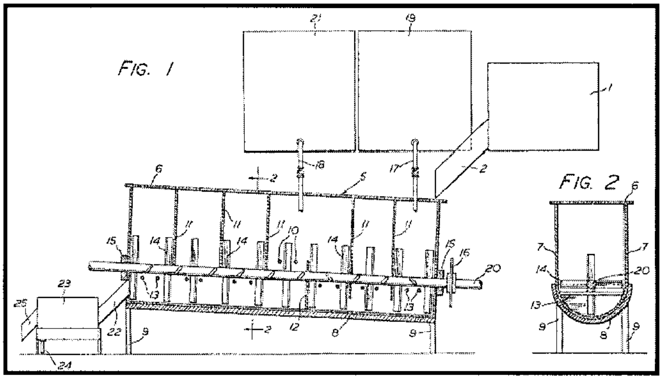

Figure 11:
Equipment for precipitation of Cellulose Acetate, forming low-density Cellulose Acetate[17]
The dope is first diluted (17) and then precipitated (18) during agitation.
1: Dope feed
19/21: Dilute Acetic Acid
14/20: Agitator
25: Slurry discharge

High density Cellulose Acetate is produced by extrusion of Cellulose Acetate solution in diluted Acetic Acid with a means for cutting the strands to form more or less regular pellets (see Figure 12). Especially after precipitation of high density Cellulose Acetate, it is necessary to harden the pellets before washing. This is accomplished by longer residence time of the pellets in dilute Acetic Acid for diffusion of water and Acetic Acid through the solid skin.

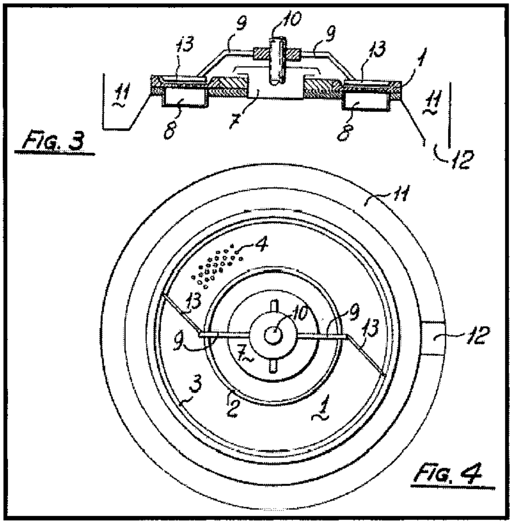

Figure 12:
Equipment for precipitation of Cellulose Acetate, forming high-density Cellulose Acetate [18]

The dope is extruded through holes (4), cut by rotating knifes (13) and flushed away by dilute Acetic Acid.

8: Dope feed
4: Plate with holes
7: Dilute Acetic Acid feed
9/13: Rotating knifes
11/12: Slurry discharge

Washing:

The classical process is batch washing using agitated vessels with a perforated bottom. The precipitated and hardened acetate particles are separated from the 30% Acetic Acid by filtration, forming an acetate layer on the bottom of the vessel. Then this cake is washed batch-wise by percolation of Acetic Acid with a lower concentration, coming from another batch, which is already washed once more. This quasi-countercurrent process allows minimizing water consumption. Acetic Acid from the first washing is used for precipitation. The washing is complete when a certain pH of the extract is reached. Then the Cellulose Acetate is resuspended in the water by the agitator and pumped to the dewatering section.

More efficient are processes using equipment, which extract the Acetic Acid from the precipitated Cellulose Acetate in real countercurrent mode, e.g. a rotative extractor. Other suitable equipment are washing towers or countercurrent belt extractors.

Drying:
The first step in drying is usually draining free water followed by mechanical squeezing of the wet acetate, containing 70 - 90% water. This mechanical dewatering reduces the energy consumption of the subsequent thermal drying step. Different equipment can be used to dewater the acetate particles. Most industrial processes use a roller press, which was originally developed for sugar cane processing. Dewatering screw presses or centrifuges can also be used. Water concentration after mechanical squeezing is in the range of 35 to 45%.

Thermal drying of Cellulose Acetate can be done in many different types of dryers. Most common in the acetate industry are rotary dryers with steam-heated tubes for conductive heat transfer and hot air for transporting the water out of the dryer. Drying usually is done at atmospheric pressure at air temperatures below 100°C. Over-drying of Cellulose Acetate could create deactivation, resulting in incomplete dissolution in acetone. Adequate precautions are required to avoid dust explosions, since high concentrations of acetate dust in air could be explosive.

3.2.6 Dilute Acid treatment

During precipitation, especially when producing low-density flakes, small particles and fibers are produced. In order to avoid sedimentation in storage tanks and plugging extraction columns in Acetic Acid recovery, these suspended solids need to be separated by means of filtration, sedimentation, or centrifugation.

There are different impurities dissolved in 30% Acetic Acid. Due to the different solubility behavior at lower Acetic Acid concentrations, they could precipitate during the extraction step in Acetic Acid recovery, where the concentration decreases from 30% Acetic Acid to almost 0%. It is also possible that these impurities are extracted by the solvent and need to be separated from the concentrated acid as waste, instead of being discharged with the raffinate to the wastewater. These impurities are mainly Cellulose Acetates with short chain length and/or low degree of substitution. In order to avoid the above-mentioned problems some plants use a hydrolysis step to destroy them [19]. By lowering the pH and holding the dilute acid at elevated temperatures (80 to 100°C) for several hours, these impurities are hydrolyzed and degraded, so that they are soluble in water. A part of the bound Acetic Acid is recovered and the discharge of solid waste can be avoided.

3.2.7 Acetic Acid recovery

Liquid/Liquid-Extraction

The first step of Acetic Acid recovery is a Liquid/Liquid-Extraction by a solvent in countercurrent extraction columns. There are many different processes using different solvents, for example Di-Ethyl-Ether, MTBE, Iso-Butyl-Acetate, Ethyl Acetate, Benzene ...). The solvent should have the following properties: Minimal solubility in water, high selectivity, low energy cost for recovery, non-toxic and chemically inert.

Recovery of solvent (Stripping of raffinate, rectification of extract phase)

The raffinate of the Liquid/Liquid-Extraction contains low amounts of Acetic Acid, that were not extracted, salts, and sugars from Cellulose Acetate production and some dissolved solvent. This solvent must be recovered for economical and environmental reasons. It is done in a stripping column, heating the raffinate to higher temperatures and stripping out the solvent. After condensation, this minor part of the solvent is recycled to the Liquid/Liquid-Extraction.

The extract, the solvent with the extracted Acetic Acid and some water, overflows to another rectification step, where the solvent is separated from the Acetic Acid/water mixture. The solvent condensates and is recycled to the Liquid/Liquid-Extraction.

Purification (Rectification, purge of entrained high boilers)

After separation of solvent from the mixture Acetic Acid and water, the Acetic Acid needs to be concentrated close to 100%. Depending on the solvent chosen for the extraction, there are different processes. With Di-Ethyl-Ether and MTBE, this purification is done in a separate rectification column, producing a lower concentration Acetic Acid on top of the column. Other solvents form an aceotrope. In that case, the purification is done together with recovery of the solvent in one column.

In either case, there needs to be another purification step to eliminate high boiling impurities that were entrained by the solvent in the extract of the Liquid/Liquid-Extraction. That can be accomplished by evaporating the Acetic Acid before or after the final rectification column. The impurities must be purged and treated before disposing them.

Energy recovery

As mentioned above, acid recovery is the biggest energy consumer of the whole Cellulose Acetate process. In order to minimize total steam usage, heat recovery by indirect heat exchangers is applied to streams with high temperatures. The recovered energy can be used within the recovery line or for other consumers. Details of heat recovery depend strongly on the solvent used for extraction and the local situation.

Wastewater treatment

After stripping off the solvent, the bottom product of Liquid/Liquid-Extraction is usually sent to waste water treatment. It contains mainly:

- organic and inorganic components from wood pulp
- short chain or low DS acetate
- salts formed in Acetylation and Hydrolysis
- traces of Acetic Acid
- traces of the solvent

Depending on local situation, it needs to be neutralized or otherwise treated, before sending it to the wastewater treatment.

3.2.8 Acetic Anhydride production

A typical process to convert Acetic Acid to Acetic Anhydride is the Wacker process:

Acetic Acid is evaporated and heated up to temperatures of around 750°C in a cracking furnace. Under vacuum in the presence of catalysts, it reacts mainly to Ketene and water. The water, together with unconverted Acetic Acid, is separated from the Ketene by condensation and needs to be recovered.

The ketene so produced is reacted with Acetic Acid to give Acetic Anhydride. This crude Acetic Anhydride contains an excess of Acetic Acid, and small quantities of low boilers, high boilers and color products that need to be separated, before the Acetic Anhydride can be used again for acetylation.

Many other processes can be used to convert Acetic Acid to Acetic Anhydride.

[1] US 2,415,949 *Holloway et al.* **[1947]** Rayonier Inc.
[2] US 5,036,900 *Burley et al.* **[1991]** Courtaulds PLC
[3] Kirk-Othmer, "Encyclopedia of Chemical Technology" Vol. 10, p.607
[4] US 1,955,836 *Schneider* **[1934]** Celanese Corporation
[5] DE 739.752, *Engelmann* **[1943]** Lonza Werke
[6] US 1,566,398 *Grillet* **[1934]** Societé Chimique des Usines de Rhône
[7] GB 1.139.150 **[1966]** Societé Rhodiaceta
[8] DE 493.101 **[1928]** Societé Chimique des Usines de Rhône
[9] US 2,516,859 *Doras* **[1950]** Societé Rhodiaceta
[10] US 4,590,266 and US 5,928,613, *Yamashita* **[1986/1989]** Daicel Chemical Industries, Ltd.
[11] US 3,767,642 *Campbell et al.* **[1973]** Celanese Corp.
[12] US 4,306,060 and 4,439,605, *Ikemoto/Yabune* **[1981/1989]** Daicel Chemical Industries, Ltd
[13] Personal information, 29.9.2003
[14] US 4,342,865 *Brewer et al.* **[1982]** Eastman Kodak Company
[15] US 2,790,796 *Robin et al.* **[1957]** Societé Rhodiaceta
[16] US 5,364,935 *Cox et al.* **[1994]** Eastman Chemical Company
[17] GB 532.949 **[1939]** British Celanese Ltd
[18] US 3,493,992, *Garetto et al.* **[1970]** Rhodiatoce S.p.A
[19] FR 624.244 **[1926]** Societé Chimique des Usines de Rhône