

Purity of processed cellulose fibers

Viscose / rayon fibers are produced according to the viscose process. As the natural polymer cellulose, which is mainly isolated from wood, cannot be directly transformed into textile fibers or other cellulosic products, such as cellophane, sponges or filaments, by simple melt spinning processes it has to take a detour through temporary derivatization, which allows the spinning (shape-forming) process.

The derivatization reaction uses the reaction with sodium hydroxide lye and carbon disulfide under formation of dithiocarbonic acid esters (xanthogenic acid esters, xanthogenate group) which exists only in the form of the sodium salt under alkaline conditions in the viscose spinning dope. Hence, these esters are rather labile which is for instance seen by various transesterification reactions along and between cellulose chains in the dope.¹ In this transesterification process the ester is migrating from one cellulosic hydroxyl to a neighboring hydroxyl group of an anhydroglucose unit. The xanthogenate is only reasonably stable under alkaline conditions and at low temperature. It slowly decomposes already upon storage over several hours. The analysis of xanthogenate groups and their distribution is highly hindered by this instability effect and requires different types of stabilization reactions² to be carried out at all.

This inherent lability of xanthogenate groups (dithiocarbonic acid ester) on cellulose is very well documented in literature³ and common knowledge among cellulose chemists. The free xanthogenic acid is a weak and unstable acid with a half live of only 28s at 20°C and 120s at 2°C.⁴

During regeneration of pure cellulose, the dithiocarbonic acid is immediately cleaved off in the acidic spinning bath and pure, non-derivatized cellulose is formed. The acidic conditions of the spinning bath prevent a survival of the derivative. While the polysaccharide is regenerated chemically as pure cellulose, the xanthate group forms different sulfur-containing products. Several of them can be temporarily and partially trapped by the cellulose fiber by surface adsorption, and are removed in a subsequent washing step. Any sulfur traces on the fiber, if detectable at all, would mainly result from inorganic hydrolysis products of the xanthogenates adsorbed to the cellulose, but not from residual xanthogenates or other derivatives of the cellulose. Already 0.05 % of residual sulfur compounds (notably not in the form of a xanthogenate, but as degradation products) would cause a dull and hard touch to the textile and an opaque, matt appearance⁵, which would be a quality issue for any textile fiber and is thus strictly avoided. Hence, the average sulfur content⁶ of a viscose fiber is 156 ±40 ppm (N=8), this corresponds well to other specifications of viscose fibers of 140 ppm.⁷

Still, if we assume based on an statement with unidentified source, that residual xanthogenate groups survive on the fiber we can hypothetically calculate the resulting degree of modification, to be precise the degree of substitution with sulfur-containing groups. If we base this calculation on 200 ppm sulfur, we would arrive at one xanthogenate group per ~ 2000 anhydroglucose units, taking the molar mass of viscose with a DP of 370⁸ into account. This means we would have one substituent every fifth cellulose chain on average! It is pointed out again that this value is based on the unreasonable assumption that 200

¹ Philipp, B., Lin, K. *Faserforsch. Textiltech.* **1959**, *10*, 555

² Russler et al., *Holzforschung*, **2006**, *60* (5), 467-473.

³ Götze, K. (Eds.) *Chemiefasern nach dem Viskoseverfahren*. 3rd Edition 1967, Springer, Berlin, Heidelberg, p.401 ff.

⁴ Du Rietz, C. *Svensk. KemTidskr.* **1957**, *69*, 6

⁵ Götze, K. (Eds.) *Chemiefasern nach dem Viskoseverfahren* Third Edition 1967, Springer, Berlin, Heidelberg, p. 583.

⁶ ISO EN 17294-2, based on ICP-MS

⁷ <http://www.chinafiber.com/viscose/> accessed 09.04.2020

⁸ Siller, M. et al. *Cellulose* **2014**, *21* (5), 3291-3301.

ppm organic sulfur (e.g. xanthogenate groups) would be present, which is not the case. Instead, the actual nature of the 200 ppm residual sulfur is mainly inorganic (sulfate), i.e. ash, from the zinc sulfate/ sulfuric acid containing spinning bath.

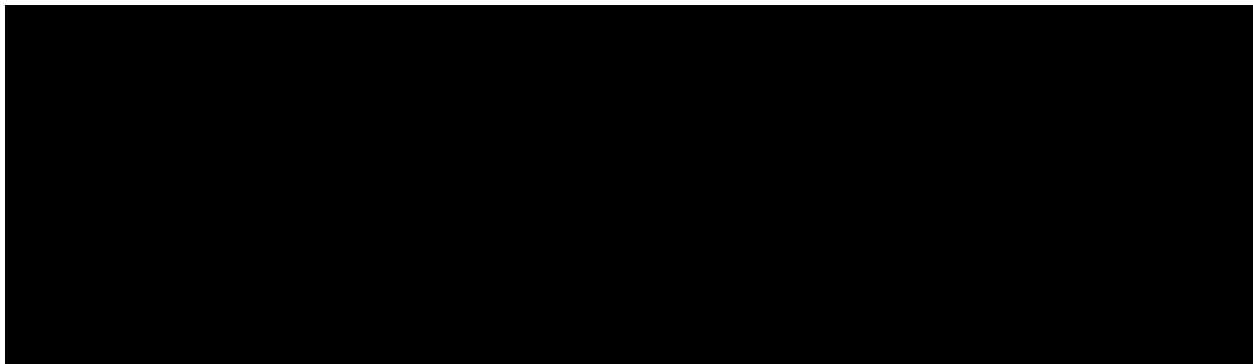
To address purity of the end product cellulose after the viscose process the sugar composition provides reliable data. After total hydrolysis and after methanolysis⁹, the latter being a method to specifically address residual hemicelluloses in the fiber, a total sugar content between 98-99 % are reached, with residual hemicelluloses of about 1 %, the rest being mainly inorganic components (ash). These numbers are fully comparable to cleaned cotton (98-99% glucan). Raw cotton consist of 93 % glucan (94.3 total sugars), 1% ash based on the very same analysis method.¹⁰

The degree of carbonyls measured by a fluorescence labeling approach¹¹ corresponds to the number of reducing end groups as deduced from SEC, so the degree of additional modification is fully comparable to cotton.

Based on all available data, viscose (rayon) fibers are very pure cellulose fibers with no residual derivatives present along the cellulose chain, consisting of 99 % polysaccharides, with the remainder being inorganic compounds (ash), and an overall composition and purity completely comparable to purified cotton.

With the above data we can safely state that viscose is a very pure cellulose fiber which therefore should not be considered as chemically modified.

Please don't hesitate to contact us if there are any further questions.



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⁹ Sundberg A. et al. *Nordic Pulp and Paper Research J.* **1996**, 4, 216

¹⁰ Silbermann S. et al. *Carbohydr. Polym.* **2017**, 178, 302

¹¹ Röhrling J. et al. *Biomacromolecules* **2002**, 3 (5), 969