Neutral Sulfite Treatment of Lignocellulosic Pulps

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Birch and eucalyptus kraft pulps were treated with sulfite solutions in neutral conditions (pH 7) at 170 °C for 60 min and at 190 °C for 180 min. The pulps were analyzed for kappa number, viscosity, carbohydrate composition, and optical properties. Additionally, UV resonance Raman (UVRR) spectroscopy was applied to collect information on the contents of hexenuronic acid (HexA), lignin, and its phenolic hydroxyl groups. The sulfite treatments resulted in (i) depolymerization and partial dissolution of cellulose, (ii) partial dissolution of xylan and substantial decrease in its HexA content, and (iii) removal of the major part of lignin and increase in its phenolic hydroxyl group content. The extensive removal of HexA and depolymerization of cellulose by neutral sulfite were unexpected phenomena that have not been previously reported. According to their degree of polymerization (DP), the pulps were mainly in the form of microcrystalline cellulose after the more drastic treatments.

Keywords: Cellulose; Hexenuronic acid; Kraft pulp; Lignin; Microcrystalline cellulose; Phenolic hydroxyl group; Sulfite; UV resonance Raman spectroscopy

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INTRODUCTION

The idea of a pulp mill being a forest biorefinery, where wood is converted into several value-added chemicals (van Heiningen 2006; Liu and Amidon 2009), has gained an increasing amount of attention during the past few years. Additionally, the growing interest to reduce oil dependency in all areas and move society towards a green economy, where most products would originate from sustainably-managed renewable resources, has promoted increased research activity related to lignocellulosics. Slight process modifications with a turnover from simple pulp producers to producers of pulp, transport fuels, and chemicals could be the key into new, profitable markets.

Despite the numerous alternatives, ethanol is the main liquid biofuel produced so far; governmental commitments to mitigate climate change by diminishing CO_2 emissions of fuels as well as the desire to provide alternative outlets for agricultural producers ensure that the demand of biofuels will increase in the future (Pu *et al.* 2008, Mussattoa *et al.* 2010). The first step in production of ethanol, as well as numerous other biobased chemicals, is hydrolysis of polysaccharides into sugars that can be further converted (Ragauskas *et al.* 2006).

Furthermore, carbohydrate sources can be divided in three main categories based on their different accessibility to produce biochemicals (Mamman *et al.* 2008; Mussattoa *et al.* 2010): 1) simple sugars from sugarcane, sugar beet, sorghum, wheat, and molasses (conversion not needed); 2) starches from grains like maize, wheat, or root crops such as cassava; and 3) lignocellulosic biomass from woody material, straw, agricultural waste, and crop residues. Starch containing grain crops, like sugar crops, have a higher value for food and feed applications (Mamman *et al.* 2008). There are also many ethical questions to address.

Because many animals (including humans) can digest starch but not cellulose, starch will likely prevail and provide a unique and important role in agriculture. On the other hand, cellulose, hemicellulose, and lignin are the three most abundant polymers in nature, and the effective conversion of these to value-added materials and chemicals depends on our ability to manipulate their chemistry and biochemistry (Pu *et al.* 2008, Sun *et al.* 2009). Elevating costs of chemicals and materials derived from petroleum together with increasing environmental awareness has prompted an escalating amount of research activities related to conversion and derivatization of lignocellulosics (Clark *et al.* 2009). Additionally, compared to other feedstocks including fossil (oil, natural gas, coal) and renewable ones (sugarcane, corn), lignocellulosic feedstocks are cheap (Pu *et al.* 2008, Tunc and van Heiningen 2008).

Our original target in this study was to increase the reactivity and solubility of hardwood kraft pulp lignin by demethylating it with a neutral sulfite treatment. Demethylation introduces new phenolic hydroxyl groups, and thus new reactive sites are incorporated into the structure of the lignin. Some demethylation reactions occur naturally during pulping and bleaching, and the reaction of sulfite and lignin model compounds in a neutral medium has been reported to demethylate them under conditions similar to neutral sulfite pulping (Croon and Swan 1964). Demethylation produces methane sulfonic acid as the main cleavage product (Gellerstedt and Gierer 1968). Furthermore, the kinetics of the reaction have been studied at 170, 180, and 190 °C (Gierer and Koutek 1969).

EXPERIMENTAL

Materials

Unbleached birch kraft pulp (kappa number 15.4, HexA content 51 mmol/kg, viscosity 1350 mL/g, brightness 36 %) was obtained from a Finnish pulp mill, whereas the unbleached eucalyptus kraft pulp (kappa number 17.4, HexA content 67 mmol/kg, viscosity 1240 mL/g, brightness 30 %) was from a pilot trial by Andritz.

Sulfite Treatments

All treatments were carried out in neutral sulfite solution (0.1 M $NaHSO_3$ + 0.9 M Na_2SO_3; pH set to 7.0). Batches of 30 g o.d. pulp were homogenized and added to 2-liter stainless steel vessels with 1000 mL of sulfite solution. The vessels were closed and fixed into a rotating air bath digester. Heating time for all experiments was 60 min until the maximum temperature (*i.e.* 170 °C or 190 °C) was reached. After 60 min or 180 min (maximum) had elapsed, the vessels were cooled down in cold water, opened, and the pulps were filtered in a Büchner funnel; pH of the filtrates was measured. The pulps were washed in the Büchner funnel with deionized water. The pulps were homogenized and their dry matter contents were determined.

Laboratory Sheets

Standard laboratory sheets, 60 g/m^2, (ISO 5269-1:2005(E)) were prepared from untreated pulp as reference (R) and from sulfite-treated pulp (S).

UV Resonance Raman (UVRR) Spectra

The UVRR spectra were obtained with a Renishaw 1000 UV Raman spectrometer, which was connected to a Leica DMLM microscope and an Innova 300C FreD frequency-doubled Ar+ ion laser. The excitation wavelength of the laser was 244 nm, the power output was 10 mW, and the measuring transmittance was 25%. The beam was directed through a 40× objective on the pulp sheet that was rotated to avoid burning. The applied measuring time was 15 s. Three parallel measurements were collected from each sample and the average spectrum was used to analyze the results. The Raman spectra were baseline-corrected to zero at two points (~800 and ~2000 cm^{-1}) and normalized to 1093 cm^{-1} cellulose band. Dry sheet samples as well as sheet samples moisturized with pH 6 phosphate buffer solution or 0.2 M NaOH were measured. The exact aromatic band position at ~1600 cm^{-1} was obtained as the shift at zero value of the first derivative spectrum.

Hexeuronic Acid and Lignin Contents

The content of hexeuronic acid (HexA) in the pulps was analyzed separately with two different methods. The pulps were hydrolyzed by mild acid under standard conditions, and 2-furoic acid liberated from HexA was determined spectrophotometrically (Tenkanen *et al.* 1999). HexA contents of the pulps were additionally calculated from their UVRR spectra using the relative band intensities of HexA (~1650 cm^{-1}) and cellulose (1093 cm^{-1}) (Jääskeläinen *et al.* 2005). Similarly, the content of lignin in the pulps was obtained through relative band intensities of lignin (~1600 cm^{-1}) and cellulose (1093 cm^{-1}) (Jääskeläinen *et al.* 2005).

Kappa Number, Viscosity, and DP of Cellulose

Viscosity (SCAN-CM 15:99) and kappa number (SCAN-C 1:00) were analyzed according to standard methods. Some viscosities were so low that a calibration viscometer had to be applied in order to get reliable results (sulfite-treated samples). Degree of polymerization (DP) of cellulose was estimated with the Mark-Houwink-Sakurada equation,

$$[\eta] = k' DP^{\alpha} \tag{1}$$

where $[\eta]$ is viscosity, k'= 1.33, and α=0.905.

Carbohydrate Composition

Carbohydrates were analyzed with two-stage acid hydrolysis combined with HPAEC according to a standard from the National Renewable Energy Laboratory of the U.S. Department of Energy, called “Determination of structural carbohydrates and lignin in biomass,” technical report NREL/TP-510-42618. The only exception to the standard was that sample pH was not set prior to HPAEC analysis.

Optical Properties

Optical properties including ISO-brightness, CIELab coordinates, light scattering and absorption, and opacity were collected with an Elrepho spectrophotometer (Lorentzen & Wettre) from the sample sheets.

RESULTS

UVRR Spectra

In the UV resonance Raman (UVRR) spectra of cellulosic pulps, the aromatic band at 1604 cm^{-1} is assigned to lignin (Halttunen *et al.* 2001); when the amount of lignin in the sample decreases, the intensity of this band relative to the cellulose band at 1093 cm^{-1} goes down. Thus, removal of lignin by neutral sulfite was clearly visible in all spectra (Figs. 1 and 2).

Previously it was reported that the pH of aqueous solutions of phenolic lignin monomers affect their Raman spectra (Warsta *et al.* 2012). UVRR spectra of the kraft pulps confirmed that pH has a substantial effect on the Raman scattering of lignin (Fig. 2). While increasing pH appeared to increase the Raman scattering intensity of phenolic monomers (Warsta *et al.* 2012), with the pulp samples the trend was mainly the opposite, although not always consistent. Most pulp samples (10 of 12) analyzed after wetting with 0.2 M NaOH gave slightly lower maximum intensities (normalized to the cellulose band at 1093 cm^{-1}), than the same samples analyzed at pH 6. Most probably this anomaly was observed because only a fraction of all lignin units are phenolic.

Phenolic Hydroxyl Groups and Guaiacyl Units of Lignin

It was reported earlier that the content of phenolic hydroxyl groups in lignin can be quantified through measuring UVRR spectra at neutral and alkaline pH (Warsta *et al.* 2006, Lähdetie *et al.* 2007, Warsta *et al.* 2012). Thus, the pH-induced aromatic band shift (pH 6 buffer *vs*. 0.2 M NaOH) was applied to calculate the actual phenolic hydroxyl group content according to Warsta *et al*. 2006 (Table 1). The neutral sulfite treatment increased the content of phenolic hydroxyl groups in the residual lignin, which was expected, since sulfite is known to demethylate lignin in the conditions applied.

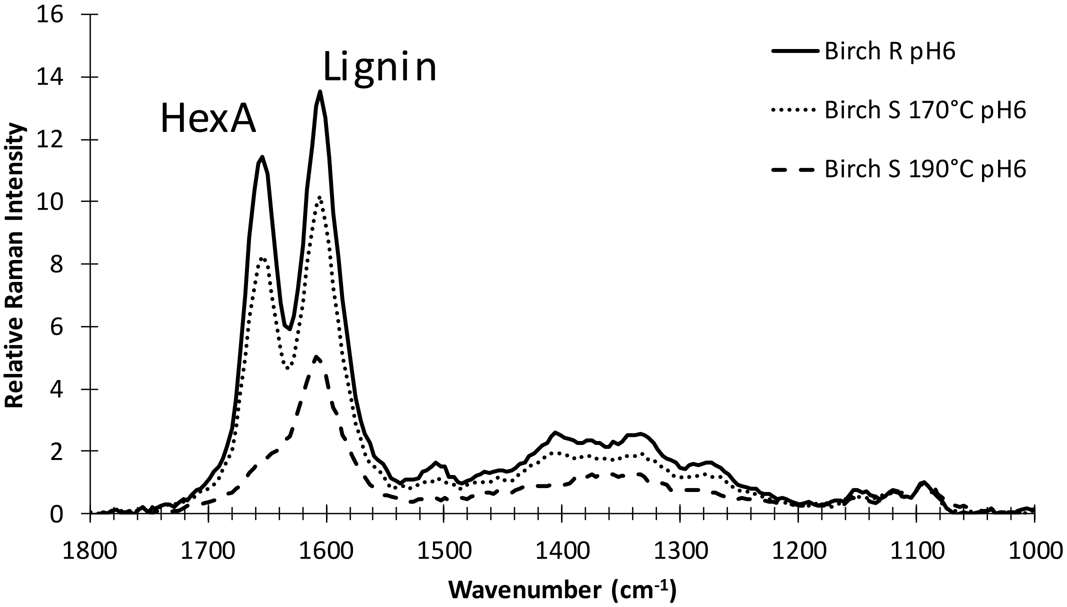

Fig. 1. UV resonance Raman spectra of reference (R) and neutral sulfite (S) treated birch kraft pulp sheets moisturized with pH 6 buffer solution. The sulfite treatments were carried out for 60 min at 170 °C or 180 min at 190 °C. The spectra were normalized relative to the cellulose band intensity at 1093 cm^{-1}.

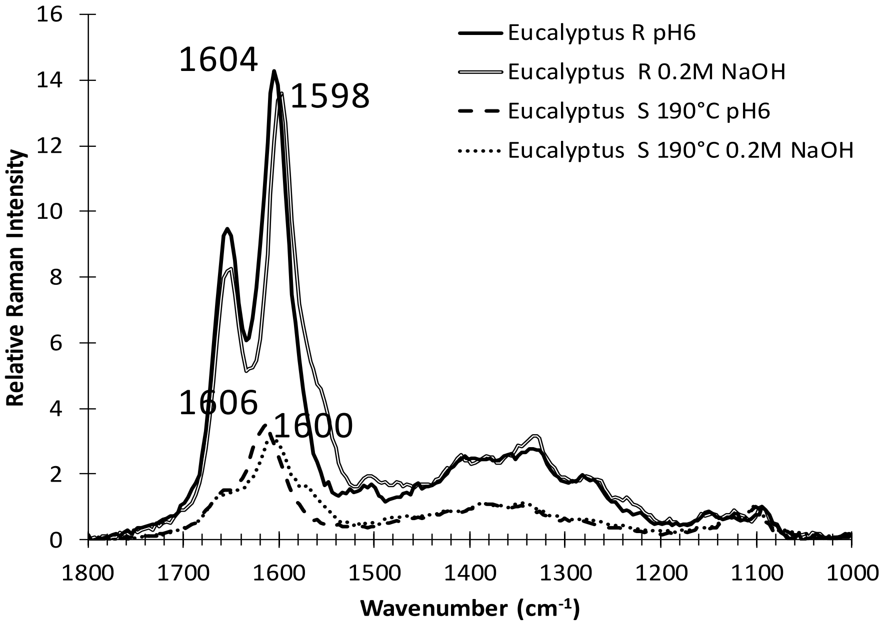

Fig. 2. UV resonance Raman spectra of reference (R) and neutral sulfite (S) treated eucalyptus kraft pulp sheets moisturized with pH 6 buffer solution or 0.2 M NaOH. The sulfite treatments were carried out for 180 min at 190 °C. The aromatic bands are labeled for their exact position (cm^{-1}). The spectra were normalized relative to the cellulose band intensity at 1093 cm^{-1}.

Table 1. Properties of Unbleached Birch and Eucalyptus Kraft Pulps Before and After Neutral Sulfite Treatment of 180 min at 190 °C

	Reference birch pulp	Sulfite-treated birch pulp	Reference eucalyptus pulp	Sulfite-treated eucalyptus pulp
Kappa number	15.4	5.4	17.4	4.3
Lignin kappa number[a]	10.7	4.6	11.5	3.5
Lignin content (%)[b]	1.8	0.8	1.9	0.6
Phenolic groups (mol/kg lignin)[c]	3.7	4.3	4.0	4.5
HexA (mmol/kg)[d]	47	8	65	8
HexA (mmol/kg)[e]	55	10	69	10
ISO Brightness (%)	36	56	30	54
Light absorption coefficient (m^2/kg)	8.6	4.0	20.1	6.1
Light scattering coefficient (m^2/kg)	33.3	51.9	46.9	57.9
Viscosity (mL/g)	1350	180	1240	180
DP of cellulose	2100	230	1910	230

a. According to Li and Gellerstedt (1997)
b. Calculated according to Jääskeläinen *et al.* (2005) (UVRRS)
c. Calculated according to Warsta *et al.* (2006) (UVRRS)
d. Through acid hydrolysis
e. Calculated according to Jääskeläinen *et al.* (2005) (UVRRS)

Besides the shift in the main aromatic band at ~1600 cm^{-1}, a shoulder at ~1560 cm^{-1} was visible in the UVRR spectra of sheets moisturized with 0.2 M NaOH (Fig. 2). This overlapping band is typical for phenolic guaiacyl units of lignin (Warsta *et al*. 2012). Because the shoulder was relatively more intense for the neutral sulfite-treated pulp in comparison with the reference, the sulfite treatment increased, as well as the content of phenolic guaiacyl units in the residual lignin.

Table 2. Properties of Unbleached Birch and Eucalyptus Kraft Pulps Before and After Neutral Sulfite Treatment of 180 min at 190°C

	Untreated birch pulp	Sulfite-treated birch pulp	Untreated eucalyptus pulp	Sulfite-treated eucalyptus pulp
Cellulose (as anhydroglucose)	76.5	52.2	82.7	62.2
Xylan (as anhydroxylose)	18.7	12.3	15.3	11.1
Mannose	0.3	0.0	0.1	0.0
Lignin	1.8	0.5	1.9	0.4
HexA	0.9	0.1	1.1	0.1
Total (without Hexa)	98.2	64.9	101.1	73.9

Removal of HexA

UVRR spectra of hardwood pulps possess a band at ~1655 cm^{-1} that is assigned to hexenuronic acid (HexA), which is a major substituent on residual xylan in kraft pulps (Halttunen *et al*. 2001). The HexA content was calculated from the UVRR spectra according to Jääskeläinen *et al*. 2005. The neutral sulfite treatment diminished the amount of HexA remarkably, which was unexpected (Figs. 1-2, Table 1). At the harsher conditions at 190 °C HexA was almost totally removed.

To confirm the trend in the Raman spectra, HexA was also analyzed with a wet chemical method, which gave similar results (Table 1). Although the two methods gave somewhat different absolute values, the relative changes were comparable. It has already been shown that HexA can be released from xylan in acid and more slowly in alkaline conditions. Degradation of HexA by a strong nucleophile (sulfite) in neutral conditions has not yet been reported.

Kappa Number and Optical Properties

The neutral sulfite treatment significantly decreased the kappa number of the pulps which can, in part, be attributed to the degradation of HexA. In order to calculate the lignin contents of the pulps, the contribution from HexA was reduced from the kappa number (Table 1). The harsh neutral sulfite treatment decreased the residual lignin content by > 50% while the reduction in HexA content was significantly higher or > 80%. The more pronounced effect of neutral sulfite on HexA is also visible from the UVRR spectra (Figs. 1 and 2).

The neutral sulfite treatments significantly increased the brightness of the pulps (Table 1). In part, this was caused by the removal of lignin and its effect on light absorption. However, the sulfite treatments also led to markedly increased light scattering of the sheets which could indicate changes in the cell wall polysaccharides that are more responsible for the physical sheet properties.

Carbohydrate Composition

According to the low viscosity and yield of the extensively treated pulps, it is clear that the neutral sulfite treatments also degraded the cell wall polysaccharides through cleavage of glycosidic bonds (Tables 1 and 2). The mass balances of the pulp treatments revealed that most of the carbohydrate losses were caused by degradation of cellulose (Table 2). In addition, the extremely low level of the viscosity and low DP of cellulose indicated that the harsh sulfite treatment produced mainly microcrystalline cellulose. In the literature a DP of 225 has been reported for microcrystalline cellulose (Chakraborty *et al.* 2006); this value is very close to the DP of the sulfite-treated samples (Table 1).

The cleavage of glycosidic bonds under the conditions applied was most probably caused by a nucleophilic attack (S_N2) of the sulfite ion on either C1 or C4 of the anhydroglucose units of cellulose. Thus, as demethylation of lignin by sulfite yields methane sulfonic acid, cleavage of cellulose and hemicelluloses by sulfite could form sugar sulfonic acids. Moreover, the pulps treated under these conditions could be expected to contain sulfonic acid ($-SO_3H$) groups attached to the carbohydrates.

DISCUSSION

To our surprise, neutral sulfite treatments of kraft pulps led not only to dimethylation and dissolution of lignin, but also to extensive cleavage of hexenuronic acid (HexA) and depolymerization of cellulose. To our knowledge, such a drastic nucleophilic cleavage of glycosidic bonds by sulfite has not yet been reported.

Depolymerization of cellulose to the level of microcrystalline cellulose and the introduction of cellulose-bound sulfonic acid groups may have many potential material applications. Properties of cellulose derivatives are mainly determined by the type of functional group, although modification is possible by controlling the degree of substitution as well as the degree of polymerization of the polymer backbone (Heinze and Liebert 2001). Sulfonic acid groups ($-SO_3H$) in cellulose increase water solubility of the polymer (Knaus and Bauer-Heim 2003, Rajalaxmi *et al.* 2010). Indeed, oxidation and sulfonation of cellulose increased the water solubility of cellulose samples from 2.85 up to 28.57 g/L with high sulfonation rates (Rajalaxmi *et al.* 2010). Sulfonated cellulose can be applied, *e.g.* in the concrete industry, as a viscosity-increasing agent or as a so-called superplasticizer, which interacts with the surface of cement particles by provoking dispersion and decreasing coagulation tendency (Knaus and Bauer-Heim 2003). Furthermore, sulfonated cellulose as biocompatible and biodegradable material is well suitable for biomedical applications (Rajalaxmi *et al.* 2010).

Cellulose-SO_3H has been introduced also as a heterogenous solid acid catalyst for the synthesis of quinolines (Shaabani and Maleki 2007), α-amino nitriles (Shaabani *et al.* 2008), dibenzo xanthenes (Madhav *et al.* 2009), 2-oxazolines, 2-imidazolines and 2-thiazolines (Shaabani *et al.* 2009), tetrahydroquinolines (Kumar *et al.* 2010a), functionalized pyrrolidines (Kumar *et al.* 2010b), as well as tetrahydropyranols (Subba Reddy *et al.* 2010). In fact, it has been reported that cellulose-SO_3H makes the process economically possible for large-scale synthesis of tetrahydropyranols. Moreover, cellulose-SO_3H is suitable to catalyze esterification and transesterification in biodiesel production, and it exhibits higher catalytic performance than other conventional solid Bronsted acid catalysts (Hara 2010). In addition, cellulose sulfonate catalyzes cellulose saccharification *i.e.* hydrolysis of cellulose as efficiently as H_2SO_4. The high catalytic activity compared to other catalysts is probably explained not only by the presence of SO_3H groups, but also by the presence of OH and COOH as functional groups in the structure.

Solid acid catalysts are generally easily separated (and recycled) from the reaction liquids readily after reaction, and the chemical industry is eager to replace liquid acid catalysts with solid ones because of environmental and economic reasons (Cybulski *et al.* 2001; Sheldon and van Bekkum 2001; Yadav 2005; Hara 2010). A majority of the reported catalysts are either based on inorganic materials or functional synthetic polymers engaging in a high manufacture temperature *via* calcination or polymerization of petrochemical feedstocks (Guibal 2005). Conventional homogenous catalysts (*e.g.* HCl, KOH, and H_2SO_4) have serious limitative features due to toxicity, corrosive reagents, tedious preparation, neutralization of effluents, long reaction time, and high temperature (Shaabani *et al.* 2008; Hara 2010; Kumar *et al.* 2010a).

On the other hand, it should be noted that, in the literature, cellulose sulfate (cellulose-OSO_3H, cellulose sulfuric acid) is occasionally mixed with cellulose sulfonate (cellulose-SO_3H, cellulose sulfonic acid), which might be misleading (Shaabani and Maleki 2007; Shaabani *et al.* 2008, 2009; Madhav *et al.* 2009).

Microcrystalline cellulose (MCC) itself can be used as a reinforcement material in composites (Chakraborty *et al.* 2006). In addition, gels based on MCC have applications in several fields, such as medicine, the food industry, cosmetics, agriculture, and the paper industry (Laka and Chernyavskaya 2009). MCC has valuable properties, *e.g.* high sorption ability, viscosity regulation ability, compatibility with living tissues, and protective ability against bacteria, which enable its wide usage.

The number of publications on the reactions of sulfite and cell wall polymers in neutral conditions is very small, since the conditions for conventional pulping applications are not considered to be optimal at the neutral pH area. Therefore, data on reaction kinetics of sulfite with carbohydrates under neutral conditions is not available at the moment.

CONCLUSIONS

1. Most of the HexA was removed during the neutral sulfite treatments.
2. The neutral sulfite treatments decreased the lignin content and modified the structure of remaining lignin: the amount of phenolic hydroxyl groups was increased in the course of the treatments.
3. The viscosity of the pulps was destroyed into a low level, and the resulting pulp could no longer be considered for paper making applications. However, the degree of polymerization indicated that the carbohydrates after sulfite treatment existed mainly in the form of microcrystalline cellulose, and in neutral conditions the reactions produced cellulose sulfonic acid, which might have various applications.

4. Further studies are needed to discover the reaction kinetics and possibilities to produce cellulose sulfonic acids in neutral conditions.

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