Understanding Decay Resistance, Dimensional Stability and Strength Changes in Heat Treated and Acetylated Wood

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ABSTRACT

Reductions in hygroscopicity, increased dimensional stability and decay resistance of heat treated wood depends on decomposition of a large portion of the hemicelluloses in the wood cell wall. In theory, these hemicelluloses are converted to water and volatile furan-type intermediates that can polymerize in the cell wall. Reductions in hygroscopicity and improved dimensional stability of acetylated wood depends on esterification of the accessible hemicelluloses in the cell wall reducing hydrogen bonding with water and bulking the cell wall back to its green volume. Stability is not 100% since the water molecule is smaller than the acetyl group so water can access hydroxyl sites even when the wood is fully acetylated. The cell wall moisture content is too low in acetylated wood to support fungal attack so the initial enzymatic attack starting the colonization does not take place. The critical sugar in the hemicelluloses that may be the trigger for fungal attack is arabinose as it is the only sugar in a less stable five-member ring as compared to sugars in a stable six-membered ring. Strength properties are reduced in heat treated wood as a result of the degradation of the cell wall matrix resulting from the hemicellulose loss. Strength properties are not significantly changed in acetylated wood and acetylation results in greatly improved wet strength and wet stiffness properties.

INTRODUCTION

With an increased awareness of the fragility of our environment and the need for durability in wood products, new technologies have been developed to increase the service life of wood materials without the use of toxic chemicals. Issues of sustainability, carbon sequestration and performance converge in this search for environmentally friendly methods of wood preservation.

Heat treatments of wood and chemical modification using acetic anhydride to acetylate wood have been studied for many years and are now both commercial. Both methods result in increased decay resistance and improved dimensional stability to different degrees. Strength properties of the wood is also affected mainly by heat treatments.

HISTORY

Heat Treatments

Heating wood to improve performance dates back many thousands of years. The Kalvträsk wooden ski was bent using heat by the Saami and used in northern Sweden over 5200 years ago (Åström 1993, Insulander 1999). From hieroglyphic pictures of furniture in Egypt between 2500 and 3000 BC, there are chairs made using heat bent wood members (Rivers and Umney 2005). The Egyptians also bent wood for bows using hot water around 1900 BC as shown on tomb paintings (Ostergard 1987). In the 11th century, the Viking shipbuilders also bent wood using heat for parts of the ship (Olsen and Crumlin-Pedersen 1967). In the Norwegian stave churches, large beams were bent using heat and joined (Bugge 1953, Holan 1990). Finally, the wooden cask makers knew how to heat-bend wood 2000 years ago (Twede 2005). A picture of a wooden cask is shown on the wall of a 2690 BC Egyptian tomb (Kirby 1971). Wooden casks were also made by the Romans to store wine (Twede 2005).

In the early part of the 20th century it was found that drying wood at high temperature increased dimensional stability and a reduction in hygroscopicity (Tiemann 1915, Stamm and Hansen 1937). Later, it was found that heating wood in molten metal at temperatures between 140 and 320 °C reduced swelling in Sitka spruce by 60% and also increased resistance to microbiological attack (Stamm *et al.* 1946). They also found that the increase in stability and durability also increases brittleness and loss in some strength properties including impact toughness, modulus of rupture and work to failure. The treatments usually cause a darkening of the wood and the wood has a tendency to crack and split.

Burmester studied the effect of temperature, pressure and moisture on wood properties (1973). He found that the optimum conditions for pine were 160 °C, 20-30% moisture and 0.7 MPa pressure. He reported high dimensional stability and resistance to brown-rot fungi attack and minimal loss of strength. He named his process as FWD (Feuchte-Wärme-Druck).

More recently, Norimoto *et al.* (1993) and Ito *et al.* (1998) heated wet wood to improve dimensional stability. Inoue *et al.* (1993) heated wet wood to fix compression set in wood.

Several names have been given to the various heat treated products and treatments for wood. Including Staypak and Stabwood in the United States (using dry wood); Lignostone and Lignofol from Germany (using dry wood), Jicwood and Jablo from the UK, Thermowood in Finland (using water vapour), Plato in The Netherlands (using water), Perdure from Canada (using steam), Oil Heat Treated (OHT) from Germany (using oil) and New Option Wood/Retification in France (using nitrogen) (Hill 2006).

Acetylation

The acetylation of wood was first performed in Germany by Fuchs (1928), using acetic anhydride and sulfuric acid as a catalyst. Fuchs found an acetyl weight gain of over 40%, which meant that he decrystalized the cellulose in the process. He used the reaction to isolate lignin from pine wood. In the same year, Horn (1928) acetylated beech wood to remove hemicelluloses in a similar lignin isolation procedure. Suida and Titsch (1928) acetylated powdered beech and pine using pyridine or dimethylaniline as a catalyst to yield an acetyl weight gain of 30 to 35 percent after 15 to 35 days at 100 ºC.

Tarkow (1945) first demonstrated that acetylated balsa was resistant to decay. Tarkow (1946) first described the use of wood acetylation to stabilize wood from swelling in water. Since the 1940s, many laboratories around the world have looked at acetylation of many different types of woods and agricultural resources.

Acetylation of wood using acetic anhydride has mainly been done as a liquid phase reaction. The early work was done using acetic anhydride catalyzed with either zinc chloride or pyridine. Through the years, many other catalysts have been tried both with liquid and vapor systems. Some of the catalysts used include urea-ammonium sulphate, dimethylformamide, sodium acetate, magnesium persulfate, trifluoroacetic acid, boron trifluoride and γ-rays. The reaction has also been done without catalyst and by using an organic co-solvent. Gas phase reactions have also been reported using both ketene and acetic anhydride; however, the diffusion rate is very slow so this technology has only been applied to thin veneers (Rowell 2005). Most acetylation reactions done today are done without the use of a catalyst.

Acetylated wood is now sold by Titanwood in Arnhem, The Netherlands. It is sold under the name of accoya® and available in several species of wood in Europe, North America and Asia.

CHEMISTRY

Heat Treatment

There are a variety of thermal modification processes that have been developed. The results of the process depend on several variables including time and temperature, treatment atmosphere, wood species, moisture content, wood dimensions and the use of a catalyst (Stamm 1956, Millett and Gerhards 1972). Temperature and time of treatment are the most critical elements and treatments done in air result in oxidation reactions not leading to the desired properties of the treated wood. Wood degrades faster when heated in either steam or water as compared to dry conditions (MacLean 1951, 1953, Millett and Gerhards 1972, Hillis 1975). Stamm (1956) showed that wood heated in the presence of oxygen degraded more rapidly that wood heated in an oxygen-free atmosphere. As the treatment time increases, embrittlement of the wood increases (Yao and Taylor 1979, Edlund 2004). Generally, weight loss occurs to a higher extent in hardwoods as compared to softwoods which may be due to the higher content of acetyl groups in hardwoods releasing more acetic acid during heat treatment contributing to the acid hydrolysis (MacLean 1951, 1953, Millett and Gerhards 1972, Hillis 1975).

As the wood is heated, the first weight loss is due to the loss of water, followed by a variety of chemistries that produce degradation products and volatile gasses (Shafizadeh and Chin 1977). As the temperature increases, wood cell wall polymers start to degrade. Pyrolysis of the hemicelluloses takes place about 270 °C followed closely by cellulose. Lignin is much more stable to high temperature (Stamm 1956). In the early stages of degradation, 83% of the weight loss is water (Mitchell *et al.* 1953). The hemicellulose polymers are the first to degrade followed by cellulose resulting in the formation of furans such as furfural and hydoxymethyl furfural (Figure 1). The hemicelluloses and cellulose are also degraded to internal ethers and other rearrangement products. The optimum amount of water that can be lost is three molecules of water from two anhydroglucose units or 16.7 percent of the carbohydrate polymers or 12 percent of the wood (Stamm and Baechler 1960).

Table 1 shows the weight loss resulting from heating wood at different temperatures in the presence of moisture. As the temperature increases, so does the weight loss.

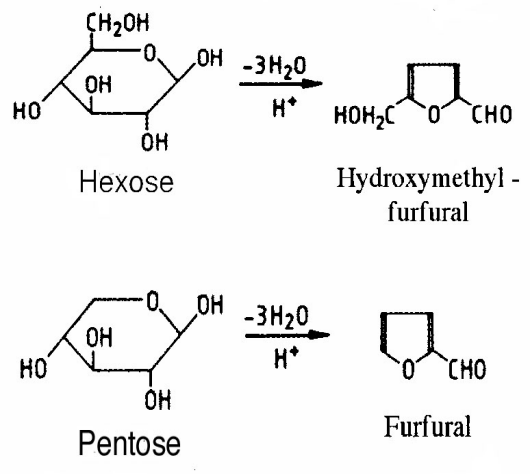


Figure 1: Formation of hydroxymethyl furfural from hexoses and furfural from pentoses as a result of heat treatments of wood.

Table 1: Weight loss due to heating wood in the presence of moisture.

Heating Temperature (°C)	Time (hrs)	Weight Loss (%)
120	2	2-3
120	10	5
180	10	10-12
190	2	4-7
190	12	5-10
200	10	10-17
220	1	6-7
235	4	25
240	0.5	7

Table 2 shows the sugar analysis before and after treating aspen with high pressure steam (220 °C) for 8 minutes. The data shows that in the very early stages of weight loss, the hemicellulose polymers are breaking down and cellulose remains unchanged. Over half of the arabinan and rhamnans are lost during this initial heating.

Table 2: Sugar analysis of aspen before and after heating at 220 °C for 8 minutes.

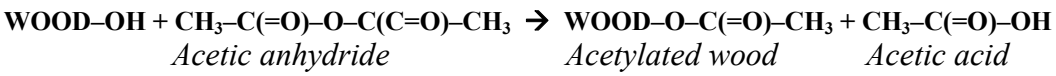
Wt Loss %	Total Carbohydrate %	Arabian %	Galactan %	Rhamnan %	Glucan %	Xylan %	Mannan %
0	61.8	0.56	0.68	0.30	42.4	16.3	1.6
2.2	59.2	0.20	0.58	0.14	42.2	14.6	1.5

Acetylated

The reaction of acetic anhydride with wood results in esterification of the accessible hydroxyl groups in the cell wall, with the formation of by-product acetic acid. The by-

product acid must be removed from the product as the human nose is quite sensitive to the odor of acetic acid. While this is easily done in the case of wood particles and fiber, it is somewhat difficult to do in solid wood.

Acetylation is a single-addition reaction, which means that one acetyl group is on one hydroxyl group with no polymerization:



Thus, all the weight gain in acetyl can be directly converted into units of hydroxyl groups blocked. This is not true for a reaction where polymer chains are formed (epoxides and isocyanates, for example). In these cases, the weight gain cannot be converted into units of blocked hydroxyl groups.

Isolated lignin reacts faster with acetic anhydride as compared to hemicelluloses and holocellulose (Kumar and Agawal 1983, Rowell *et al.* 1994). Kumar and Agawal (1983) reported that at an acetyl weight percent gain of 13.5, 86.4% of the lignin was acetylated, 21.6% of the hemicelluloses and 9.3% of the cellulose. Reacting wood at 120 °C with acetic anhydride and no catalyst, at an acetyl weight gain of 16 to 19%, theoretically about 90% of the lignin is esterified, and 25% of the holocellulose (Rowell 1982). It is assumed that 100% of the hemicellulose hydroxyl groups are substituted and no cellulose hydroxyl substituted. There may be a small amount of hydroxyls esterified on the surface hydroxyls in the amorphous regions of cellulose. This conclusion is based on the observation that pure cotton cellulose cloth can be used to hold wood fiber and no weight gain is observed in the cotton cloth after several acetylation reactions.

MOISTURE AND DIMENSIONAL STABILITY

Heat Treated

Because of the loss of hygroscopic hemicellulose polymers during heat treatment, the equilibrium moisture content (EMC) is reduced. Dimensional stability of heat treated wood was first thought to be due to a cross-linking of cellulose chains (Stamm and Hansen 1937). The furan intermediates that form (Figure 1) from the decomposition of the hemicelluloses have poor hygroscopicity and have little effect on the EMC.

Table 3: Reduction in EMC as a result of heating wood.

Wood species	Conditions	Reduction in EMC (%)	Reference
Pinus pinaster	190 °C 8-24 hrs	50	Esteves *et al.* 2006
Pinus sylvestris	220 °C 1-3 hrs	50	Thermowood handbook 2003
Eucalyptus globulus	190 °C 2-24 hrs	50	Esteves *et al.* 2006
Pinus sylvestris	Plato process	50-60	Tjeerdsma 2006

Table 3 shows a summary of recent results on EMC resulting from heat treatments from various authors. In most cases, a 50% reduction in EMC is observed. In most examples

given, the process was done in a vapor atmosphere between 190 and 220 °C with a relative humidity of 35 to 65%.

Table 4 shows the reduction in swelling of wood that has been heat treated.

Table 4: Dimensional stability of various woods as a result of heat treatment.

Wood species	Conditions	ASE (%)	Reference
Pinus pinaster	170 °C WL[1] 2%	50	Esteves *et al.* 2006
Eucalyptus globulus	190 °C WL 2%	77	Esteves *et al.* 2006
Eucalyptus globulus	200 °C WL 10%	60	Esteves *et al.* 2006
Pinus sylvestris	220 °C	40	Rapp Sailer 2001

[1] *WL = Weight loss*

Acetylated

Acetylation of wood reduces the number of hydroxyl groups that can sorb moisture by hydrogen bonding so the equilibrium moisture content (EMC) and fiber saturation point (FSP) are reduced and the dimensional stabilization increases with increasing weight gain due to acetylation (Rowell 2005). Table 5 shows the reduction in EMC and FSP and the antishrink efficiency (ASE) as a result of acetylation. Table 6 shows the reduction in EMC and Table 8 shows the dimensional stability for different species.

Table 5: Reduction in equilibrium moisture content as a result of acetylation.

Species	WPG	Reduction in EMC	Reference
Pinus sylvestris	20	50	Minato *et al.* 2003
Pinus elliotti	20	50	Hillis 1984
Populus tremula	20	50	Rowell 2005
Pinus sylvestris	20	70	Epmeier *et al.* 2004

Table 6: Antishrink efficiency of several types of acetylated wood.

Species	WPG	ASE	Reference
Pinus elliotti	15	60	Rowell 1983
Pinus sylvestris	20	70	Epmeier *et al.* 2004
Pinus strobus	22	70	Rowell 2005

DECAY RESISTANCE

Heat Treatment

As dimensional stability increases and hygroscopicity decreases in heat treated wood, resistance to decay also increases (Stamm *et al.* 1946, Stamm and Bacchler 1960). Table 7 shows the data of Stamm *et al.* 1946). A reduction in swelling over 40% results in no weight loss in the decay test. Similar results were obtained when the test fungus was *Lenzites trabea* 517 (Stamm and Bacchler 1960).

Table 7: Relationship between reduced swelling and decay resistance of white pine using* Trametes serialis *fungus. (Stamm et al. 1946)

Reduction in swelling (%)	Weight loss due to decay (%)
30-33	12
33-38	4.5
40 or more	0

Table 8 shows fungal resistance of two types of heat treated wood (Rapp and Sailer 2001). Pine (*Pinus sylvestris*) and spruce (*Picea abies*) were heated in oil or air at three different temperatures and the treated blocks were tested for decay for 19 weeks in the EN 113 (1996) decay test using *Coniophora puteana* fungus. The data shows that heating in oil is more effective in reducing attack by fungi than heating in air. This may be due to the presence of the oil in the samples.

Table 8: Fungal resistance of pine and spruce heated in oil or air.

	Oil Heated		Air Heated	
	Pine	Spruce	Pine	Spruce
Temperature (°C)	Wt loss (%)	Wt loss (%)	Wt loss (%)	Wt loss (%)
Control	40	48		
180	13	15	25.0	31.2
200	1.9	13.1	15.8	26.7
220	2.0	0.0	11.0	5.5

Welzbacher and Rapp compared different types of industrially heat treated products using several different fungi in laboratory tests and in different field and compost conditions (2007). Table 9 shows the weight loss during an EN 113 test using three different fungi. The heat treatment in oil was the most effective but it is not known the effect of the oil in the decay test.

***Table 9: Weight loss (%) of different woods and different heat-treating processes[1] due to attack by* Poria placenta, Coriolus versicolor *and* Coniophora puteana.**

Material	*P. placenta*	*C. versicolor*	*C. puteana*
Pine control	31.0	5.1	47.5
Douglas fir control	14.0	2.6	27.4
Oak control	0.8	14.3	3.9
Plato	10.0	6.8	3.7
Premium	16.0	9.0	1.9
NOW	13.3	7.8	12.2
OHT	7.4	5.6	3.4

[1] *Plato = Heat treated (The Netherlands), Premium = Heat treated (Finland), NOW = New Option Wood, OHT = Oil-heated wood.*

Resistance to decay in heat-treated wood is probably due to the loss of hemicellulose polymers in the cell wall. As was shown earlier, the most weight loss in the heating process, the more durable the heat-treated wood.

Acetylated

Over the years, several mechanisms have been put forward to explain the resistance to brown-rot fungal attack provided by acetylated wood. The earliest ideas centered around the modification of the conformation and configuration of the substrate such that the specific enzymatic attack could not take place (Stamm and Baechler 1960, Takahashi *et al.* 1989a, b, Takahashi 1996). Another theory is based on the bulking effect of the co-valently bonded acetyl group (Forster *et al.* 1997, Forster 1998). Alternatively, enzyme penetration is prevented by physical blocking of the cell wall micropores (Papadopoulos and Hill 2002, Hill 2002, Hill *et al.* 2005). Highley *et al.* (1994) showed that the smallest enzyme of a brown-rot fungus is too large to penetrate the cell wall. The average size of a cellulitic enzyme is about 5 nm and the smallest pore size in wood is < 3.8 nm. Mohebby (2003) speculated that there are very small regions in the cell wall that are not acetylated due to the size of the acetate group but that are accessible to free radicals produced by the fungi.

Table 10 shows the results of a fungal cellar test using control and acetylated flakeboard samples at increasing levels of acetyl content (Nilsson *et al.* 1988).

Table 10: Fungal cellar tests[1] of aspen flakeboards made from control and acetylated flakes.[2]

WPG	Rating at Intervals (months)[3]							
0	2	3	4	5	6	12	24	36
7.3	S/2	S/3	S/3	S/3	S/4	--	--	--
11.5	S/0	S/1	S/1	S/2	S/3	S/3	S/4	--
13.6	0	0	0	0	S/0	S/1	S/2	S/4
16.3	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0

[1]Nonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria. [2]Flakeboards bonded with 5 percent phenol-formaldehyde adhesive. [3]Rating system: 0 = no attack; 1 = slight attack; 2 = moderate attack; 3 = heavy attack; 4 = destroyed; S = swollen.

The present authors have postulated that the mechanism of decay resistance in acetylated wood is based on moisture exclusion due to the fact that the equilibrium moisture content of a highly modified wood is too low to support fungal attack, i.e. no water molecules at the site of a glycosidic bond that the fungal enzymes need for hydrolysis (Rowell 1983, Ibach and Rowell 2000, Ibach *et al.* 2000). Another idea is that the mechanism is based on the modification of the hemicellulose fraction in the cell wall. Maybe even more specific, the modification of the arabinose sugar in the hemicelluloses considering that this is an L-pentose sugar in the hemicelluloses and it is the only sugar in a strained five-membered ring. Why is this sugar present in this strained ring form? Could it be the trigger that Mother Nature uses as a point of attack to start the entire degradation process? Is the mechanism of resistance as simple as protecting arabinose from hydrolysis?

It is interesting to note that all woods contain acetyl groups: softwoods from 0.5 to 1.7% and hardwoods from 2 to 4.5%. Why they are present is unknown**.** Acetylation of wood to an acetyl level of about 17 to 20% renders the wood resistant to attack by both brown-rot, white-rot and soft-rot fungi.

Table 11 shows the loss of carbohydrates in the wood fiber. The non-acetylated fiber loses 85.8% carbohydrate with major weight loss in all sugars except the galactans. The

acetylated sample at 15% acetyl shows only 13.2% total carbohydrate loss, no loss of cellulose (glucans) but major losses of arabans and rhamnans.

Table 11: Carbohydrate analysis after brown-rot degradation of wood fiber.

WPG	Weight Loss %	Total Carbo Lost %	Araban Lost %	Galactan Lost %	Rhamnan Lost %	Glucan Lost %	Xylan Lost %	Mannan Lost %
0	51.7	85.8	87.9	71.9	90.0	83.8	90.6	92.5
15	1.4	13.2	89.0	55.2	70.0	0	38.3	42.0

STRENGTH

Heat Treated

Stamm *et al.* (1946) were the first to report a lost of mechanical properties as a result of heat treatments of wood. They heated wood at 320 °C for one minute or 150 °C for a week and found a 17 percent reduction in modulus of rupture (MOR) when heated in molten metal and 50 percent when heated in air. Under the same conditions, there was less loss in modulus of elasticity (MOE).

Mitchell (1988) found that losses in strength properties were much less when wood was heated dry as opposed to wet, with a greater loss in MOR than in MOE. Rusche (1973) found that strength losses were related to rate and extent of mass loss when heating beech and pine in the presence and absence of air at temperatures ranging from 100 to 200 °C. Losses in maximum strength and work to maximum load were greater for compression than for tension loads. Loss in MOE was only significant when the mass loss was greater than 8 to 10% and was the same for both species.

Rapp and Sailer (2001) heated pine and spruce at 180 to 220 °C for various times in air and in oil and determined MOR and MOE in a three point bending test. The highest MOE was 11,000 $N/mm^{2\ in}$ oil heating and little loss in MOE in both air and oil heating. MOR, however, decreased 30% in oil heating and impact bending strength decreased and the wood became brittle. Oil-heated wood lost about 50% and air-heating lost over 70% of the impact strength compared to controls.

Table 12 gives a summary of other data on strength changes in heat-treated wood. In all cases, there was only a small decrease in MOE but major changes in MOR depending on temperature, time and atmosphere.

Table 12: Change in MOR as a result of heat treatment of various woods.

Species	Treatment	MOR (%)	Reference
Betula pendula	Vapor, 200 °C	-43	Johansson and Moren 2005
Beech, spruce	Vapor 200 °C	-50	Yidiz *et al.* 2006
Pinus sylvestris	OHT 220 °C	-30	Rapp and Sailer 2001
Pinus pinaster	O_2 180-200 °C	-6 - -25	Esteves *et al.* 2006

Acetylated

Narayanamurti and Handa (1953) acetylated some woods from India and found a slight decrease in MOE of acetylated wood as compared to controls. The Koppers Company found that acetylated southern and ponderosa pine showed no loss of impact bending strength as compared to controls (1961). Dreher *et al.* studied the strength properties of acetylated pine, oak and maple boards. Compressive strength, hardness, fiber stress at proportional limit and work to proportional limit were higher in acetylated boards than in controls. MOR increased by acetylation in pine but decreased in oak and maple. MOE was unchanged while shear strength parallel to the grain was decreased in all three acetylated species. Table 13 shows the bending stiffness [MOE] and bending strength of [MOR] of acetylated radiate pine. The table shows strength properties are retained even after of acetylation.

Table 13: Bending stiffness [MOE] and bending strength [MOR] of control and acetylated radiata pine.

WPG	Density (Kg/m^3)	Moisture (%)	MOE (N/mm^2)	MOR (N/mm^2)
0	417	12.2	9664	43
20	492	5.2	8788	39

Finite span tensile strength of thin strips of pine and lime showed no significant difference in tensile strength between control and acetylated wood (Rowell and Banks 1987).

CONCLUSIONS

Reductions in hygroscopicity, increased dimensional stability and decay resistance of heat treated wood depends on decomposition of a large portion of the hemicelluloses in the wood cell wall. Strength properties are reduced in heat treated wood as a result of the degradation of the cell wall matrix resulting from the hemicellulose polymer degradation. In acetylated wood, reductions in hygroscopicity are due to substitution of hydroxyl groups with an acetyl group which is less hydroscopic as compared to the hydroxyl group. Increased dimensional stability in acetylated wood is due to the bulking of the cell wall back to its original green dimensional so the cell wall can not expand very much more (because of the elastic limit of the cell wall). Decay resistance of acetylated wood is due to the lowering of the cell wall moisture content becoming too low to support fungal attack so the initial enzymatic attack does not take place. The critical sugar in the hemicelluloses that may be the trigger for fungal attack is arabinose as it is the only sugar in a less stable five-member ring as compared to sugars in a stable six-membered ring. Strength properties are not significantly changed in acetylated wood and acetylation results in greatly improved wet strength and wet stiffness properties.

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