ment) of the primary particles in the powder and/or the temperature at which the compression takes place.   The variation of k with particle size has been anticipated from theoretical considerations.

The values of P_0 have been shown to be essentially independent of the condition of "age" of the compressed powders.

Compressibility data of tampered powders give insight into the degree of aging of silver bromide.

REFERENCES

(1) ATHY, L. F.: Bull. Am. Assoc. Petroleum Geol. **14**, 1 (1930).
(2) BALSHIN, M. YU: Vestnik Metalloprom. **18**, 124 (1938) (in Russian).
(3) BAXTER, G., AND HINES, M.: Am. Chem. J. **31**, 220 (1904).
(4) DALLA VALLE, J. M.: *Micrometrics*, p. 100. Pitman Publishing Company, New York (1943).
(5) GREEN, HENRY: J. Franklin Inst. **204**, 713 (1927).
(6) KOLTHOFF, I. M.: Tekniska Samfundets Handlingar **3**, 119 (1939).
(7) KOLTHOFF, I. M., AND O'BRIEN, A. S.: J. Chem. Phys. **7**, 401 (1939).
(8) ROLLER, PAUL S.: Ind. Eng. Chem. **22**, 1206 (1930).
(9) WULFF, J.: *Powder Metallurgy*, p. 45. American Society for Metals (1942).

DIMENSIONAL STABILIZATION OF WOOD[1]

ALFRED J. STAMM AND HAROLD TARKOW

Forest Products Laboratory,[2] Forest Service, U. S. Department of Agriculture

All known processes for stabilizing the dimensions of wood involve either (a) coatings which block the entrance and exit of water but do not change the hygroscopicity of the wood, (b) bulking agents which tend to keep wood in a swollen state, or (c) chemical agents which react with the hydroxyl groups of the cellulose, lignin, or both and replace them with less polar groups, thus reducing the hygroscopicity of the wood.

PREVIOUSLY REPORTED METHODS

Most of the efforts that have been made to stabilize the dimensions of wood involve the use of external or internal coatings.   Unfortunately, all known coatings that will adhere to wood allow the passage of some moisture.   Internal coatings are, in general, less effective than external coatings, as it is impossible to coat all the microscopically visible capillary structure completely.   One thick continuous surface film is more effective in blocking the passage of water than numerous imperfect internal films.   Good surface coatings, such as synthetic-

resin varnishes and aluminum paints, do retard the rate of moisture absorption sufficiently to minimize the steepness of moisture gradients in the wood and subsequently reduce the stresses which cause grain raising, warping, and checking (2, 6). They do not, however, prevent the aggravating swelling of drawers and doors that occurs during prolonged periods of high relative humidity.

Another approach to the stabilization of the dimensions of wood is to keep the wood in a partially or completely swollen state. When wood is treated with a concentrated solution of a hygroscopic salt (8) or sugar (1, 11), the chemical retains more water in the wood than would normally be retained at the prevailing relative humidity. When the wood is dried, shrinkage does not commence until the relative humidity falls below that in equilibrium with the salt or sugar solution within the cell walls (8, 11). The final oven-dry shrinkage is also reduced by an amount equal to the bulk of chemical held in the cell-wall structure. Wood so treated, however, is wet and sticky at the higher relative humidities, it is subject to leaching, and it is less strong than dry wood. For these reasons this method of stabilizing the dimensions of wood has never been commercialized.

If a water-insoluble material could be deposited within the cell-wall structure, the bulking effect might be made more practical. This can be accomplished by either of two methods: (a) replacement of water with a mutual solvent for water and the wax or resin with which the wood is to be treated, followed by replacement of the mutual solvent with the wax or resin; or (b) insolubilizing a water-soluble material within the cell-wall structure. Procedure (a) has been successfully carried out on small specimens of wood, using ethylene glycol monoethyl ether as the intermediate replacing agent and various waxes as the final bulking agent (9, 13). This method, although reasonably effective in reducing the swelling and shrinking, is, however, too involved for commercial use. The second method, by which phenolic resins have been formed within the intimate cell-wall structure of wood, has proven quite practical, using an unpolymerized phenol–formalin–catalyst mix or a water-soluble phenol–formaldehyde resinoid of sufficiently low molecular weight to penetrate the cell-wall structure and sufficiently polar to bond to the active groups of the wood (16). This treatment resulted in Impreg (16) and Compreg (17), resin-treated uncompressed wood and compressed wood, respectively, which found war use as aircraft carrier decking, housings for electrical control equipment, propellers, antenna masts, bearing plates, and forming dies, and which show promise of more extended peacetime uses.

Both phenol and formaldehyde and their initial water-soluble condensation product are selectively adsorbed by wood and, as a result, swell wood in their aqueous solutions more than wood is swollen by water alone. It is believed that, when the resin is formed by the application of heat, they remain chemically bonded to the hydroxyl groups of both cellulose and lignin. It thus appears that the dimensional stabilization of wood obtained by forming the resin within the wood is due to both a bulking effect and a chemical combination. The relative importance of each factor is still unknown.

The only dimension-stabilizing treatment thus far reported that can be explained only on the chemical basis is that obtained by heating wood under conditions such that water of constitution is lost.   Under these conditions it is believed that water splits out between two hydroxyl groups on adjacent cellulose chains and that an ether bridge is formed (10, 12, 14).   Stabilization presumably results from a combination of the reduction in hygroscopicity and the bridging.   This means of stabilizing the dimensions of wood is the cheapest so far developed, but, unfortunately, some carbonization and oxidation, which accompany the desired reaction, cause significant losses in strength properties. The strength loss can be minimized by heating the wood in the absence of air in a molten bath (10, 12).

ACETYLATION

The chief disadvantage of stabilizing the dimensions of wood by forming synthetic resins within the structure is that the resins embrittle the wood appreciably.   For some uses, such as in aircraft, this is very serious.   Efforts were therefore made to find some other bulking agent which preferably reacts with the hydroxyl groups of wood and which does not embrittle the wood.   Acetylation appeared to be a likely means of accomplishing this.

Acetylation as it is normally practiced on cellulose with acetic anhydride requires a swelling agent, such as acetic acid, to open up the structure and a catalyst, such as sulfuric acid, to promote the esterification reaction.   Mineral acids, however, promote hydrolysis and breakdown of the cellulose chains. This hydrolytic effect, if kept within bounds, is not harmful in plastic and rayon manufacture, but it would defeat one of the chief objectives of acetylating wood by breaking the structural bonds and embrittling the fiber.

Pyridine is known to catalyze the acetylation of cellulose with acetic anhydride.   It is effective, however, only when the cellulose has been previously subjected to a strong alkali treatment resulting in hydrate cellulose, or when the water in swollen cellulose is replaced by pyridine (4, 7).   This replacement is necessary, as pyridine itself is a poor swelling agent for cellulose.   Acetic acid could not be used as the swelling agent, owing to the fact that pyridine reacts with acetic acid to form pyridine acetate.   Staudinger (18) showed that acetylation of cellulose, using the pyridine replacement method of Hess (4), does not break down the cellulose chains.

Preliminary experiments on wood showed that it is unlike cellulose in that pyridine swells wood 25 to 30 per cent more than it is swollen by water.   It thus appeared that the alkali treatment or replacement steps would not be necessary. This proved to be the case.   Small sections of sugar maple about $\frac{1}{16}$ in. thick in the fiber direction were acetylated by immersing them in acetic anhydride–pyridine mixtures for various periods of time at various temperatures.   Acetyl contents of 20 per cent were readily obtained under the more favorable conditions, and reductions in equilibrium swelling to 30 per cent of normal (70 per cent antishrink efficiency).   This liquid-phase treatment, however, requires the take-up of a large excess of acetylating solution to assure uniform acetylation, followed

by subsequent removal of this large excess. Vapor-phase acetylation was hence tried. This proved equally successful in stabilizing the dimensions of wood, with much less take-up of chemical. In the acetylation of Sitka spruce, the take-up of solution was 227 per cent of the weight of the wood by the liquid-phase treatment and only 50 per cent of the weight of the wood by the vapor-phase method. In both cases a 21 per cent acetyl content resulted. Because of this the major part of the experimental work was carried out by the vapor-phase method.

Treating equipment

The preliminary vapor-phase treatments were made on small sections of wood merely suspended over the acetylation mixture in glass cylinders. Later acetylation studies were made in a wooden cabinet 26 by 22 by 18 in. that was lined with stainless steel and provided with stainless-steel steam coils near the bottom of the cabinet, and a stainless-steel pan over the coils with a drain for introducing and removing the acetylating liquid, a stainless-steel fan for circulation of the vapor given off from the pan, and glass rods located at the top of the cabinet from which the sheets of veneer to be treated were suspended. An exhaust tube to which a condenser might be connected insured the operation of the equipment at atmospheric pressure.

Treating variables

Although reasonable variations in the moisture content of the wood do not affect the rate or degree of acetylation by the vapor-phase method at atmospheric pressure, it is desirable to have the wood quite dry to avoid an excessive reaction of acetic anhydride with water. A moisture content of about 2 per cent, which is not difficult to attain commercially in veneer, was used in most of the experiments.

The rate of vapor-phase acetylation is determined by the rate of diffusion of vapors into wood. As diffusion varies as the square of the thickness, the acetylation time will increase rapidly with increases in thickness. Experience showed that the process should be confined to veneer of $\frac{1}{8}$-in. thickness or less or solid wood only a few inches long in the fiber direction to maintain practical treating times.

Species that have been successfully acetylated in veneer form are yellow birch, sugar maple, mahogany, sweetgum, yellow poplar, basswood, Douglas fir, Sitka spruce, and white spruce. Balsa was acetylated in blocks $\frac{1}{2}$ in. thick in the fiber direction. Softwoods (needle-bearing trees) required a higher degree of acetylation than hardwoods (broadleaf trees) to attain the same antishrink efficiency (percentage reduction in shrinkage) under equilibrium conditions. This is shown in figure 1 for a dense hardwood (sugar maple), a low-density hardwood (balsa), and Sitka spruce, a typical softwood. The time required to obtain a degree of acetylation that gives 70 per cent antishrink efficiency (70 per cent reduction in swelling and shirinking under equilibrium conditions) decreases with increasing temperature. At 90°C. about 6 hr. are required to

treat $\frac{1}{16}$-in. hardwood veneers to a 20 per cent acetyl content, using a vapor-generating solution of 20 per cent pyridine in acetic anhydride. A higher concentration of pyridine reduces the treating time only slightly. Softwoods, under the same conditions, require 10 to 12 hr. for adequte acetylation to attain the same antishrink efficiency (25 per cent acetyl content). With softwoods,
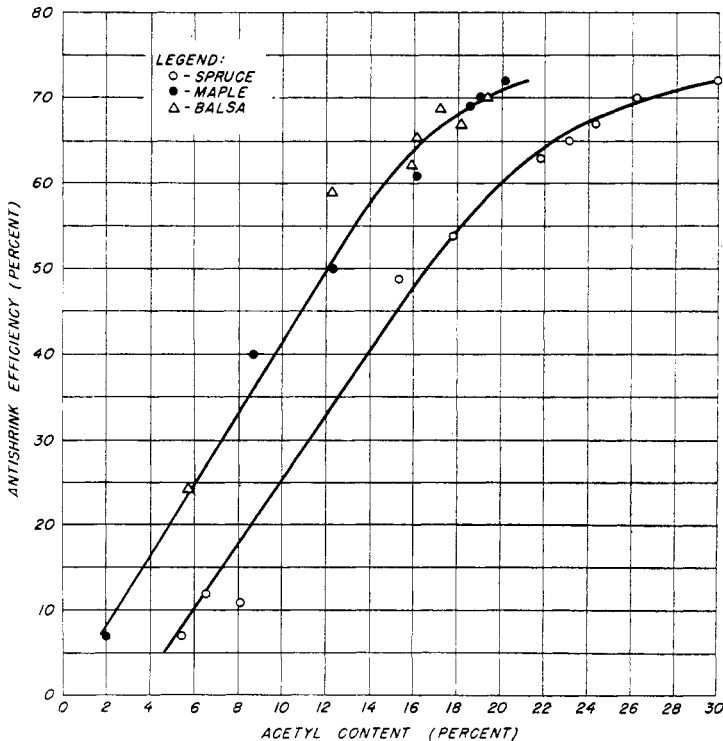

FIG. 1. Relationship between the acetyl content and the antishrink efficiency for several species of wood.

however, increasing the concentration of pyridine to 50 per cent in the liquid phase has a pronounced effect in reducing the time for adequate acetylation.

Properties

Acetylated veneer looks practically like untreated veneer. Some species appear slightly bleached, especially after exposure to ultraviolet light. Birch, on the other hand, is often but not always darkened by the treatment but bleaches on exposure to ultraviolet light. The grain of acetylated veneer may be some-

what more raised than that of untreated wood. If, however, it is pressed at as low a pressure as 100 pounds per square inch and 150°C., the surface becomes and remains extremely smooth.

Antishrink efficiencies of 70 per cent, measured between the water-soaked and oven-dry conditions or between high and low relative humidities, are readily obtained (figure 1). In some instances, antishrink efficiencies as high as 82 per cent have been obtained. These values are slightly higher than the values of 65 to 75 per cent obtainable with phenolic resins (16), 50 per cent obtainable with urea resins, and 40 to 60 per cent obtainable by heat (12). By acetylation the reductions in hygroscopicity are slightly less than the antishrink efficiencies, as is shown in table 1. Acetylated wood differs from resin-treated wood in that the communicating capillary structure is not blocked by a deposited material. Acetylated wood, therefore, takes up liquid water within the coarse capillaries about as readily as does untreated wood.

Acetylated wood shows considerable resistance to wood-destroying organisms. Acetylated balsa blocks exposed to *Poria versicolor* for three months in laboratory

TABLE 1

Percentage reduction in hygroscopicity and antishrink efficiency of acetylated Sitka spruce (30 per cent acetyl content) between the oven-dry condition and various relative humidities

RELATIVE HUMIDITY AT 80°F.	REDUCTION IN HYGROSCOPICITY	REDUCTION IN SWELLING
per cent	*per cent*	*per cent*
30	75	81
65	63	78
80	63	76
95	67	77

culture test showed no decay, whereas the untreated controls lost as much as 50 per cent of their weight. Acetylated sweetgum and yellow poplar veneer sheets, together with untreated controls, were subjected to 97 per cent relative humidity and 26.7°C. After several months the controls were coated with bluestain, whereas the treated veneer was free from stain.

Acetylated birch panels were inserted in termite-infested soil. After two years, the treated panels showed no signs of attack, whereas the controls showed moderate to bad attack. Acetylated wood was also found resistant to marine borers.

Esters of organic compounds are known to be susceptible to hydrolysis. Tests were therefore made to determine the chemical permanence of acetylated wood. Small specimens of acetylated birch were subjected to ten cycles of relative humidity change from 97 to 30 per cent at 26.7°C. for a period of four months. No change in antishrink efficiency was observed. Acetylated birch specimens were suspended over a saturated solution of sodium chloride (75 per cent relative humidity) at 80°C. for $3\frac{1}{2}$ days. No change in antishrink efficiency resulted. Thin sections of acetylated birch were immersed in a 9 per cent aqueous solution of sulfuric acid for 18 hr. at room temperature. After the

acid had been washed out, tests of antishrink efficiency and acetyl content indicated that no ester hydrolysis had occurred. When the same test was made at 40°C. the antishrink efficiency dropped from 75 to 65 per cent.

Acetylated birch panels that had been suspended in the warm saline waters of the Gulf of Mexico for two years showed no damage due to marine borers, whereas the controls were badly attacked. This resistance to borers indicates that loss of acetyl groups due to hydrolysis could not have been large.
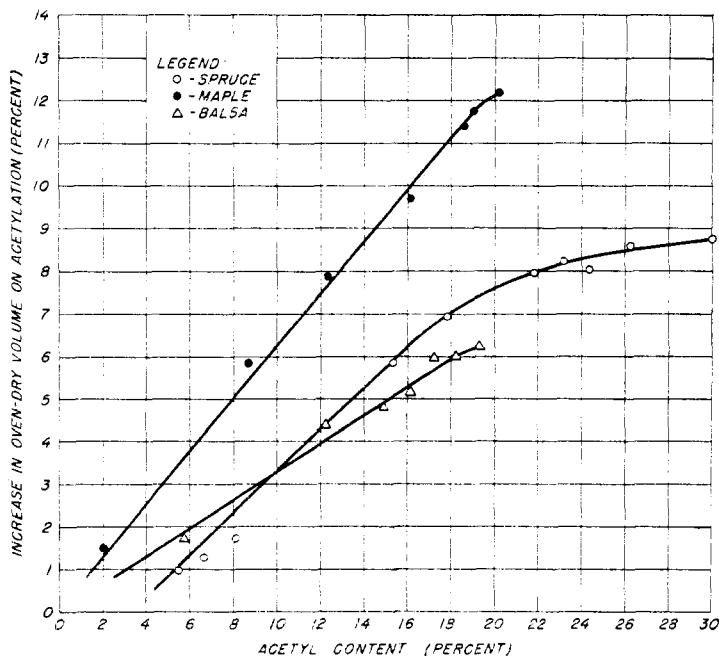

FIG. 2. Relationship between the acetyl content and the percentage increase in oven-dry volume.

Acetylation has a bulking effect upon wood. As a result, the oven-dry dimensions of wood increase with an increase in acetyl content (figure 2). The bulking effect for a fixed acetyl content also increases with an increase in the specific gravity of the wood. This is due to the facts that bulking is directly proportional to the amount of acetyl groups taken up by the cell-walls, and that any fixed acetyl content on a weight basis means a higher acetyl content per unit volume of wood for the heavier woods. Because of this, a species with high specific gravity is increased less in specific gravity as a result of a fixed degree of acetylation than a species of lower specific gravity (figure 3). At an acetyl

content of 20 per cent, for example, the oven-dry specific gravity of maple is increased by 8 per cent, that of spruce by 12 per cent, and that of balsa by 14 per cent. When based on the weight and volume under normal conditions, the
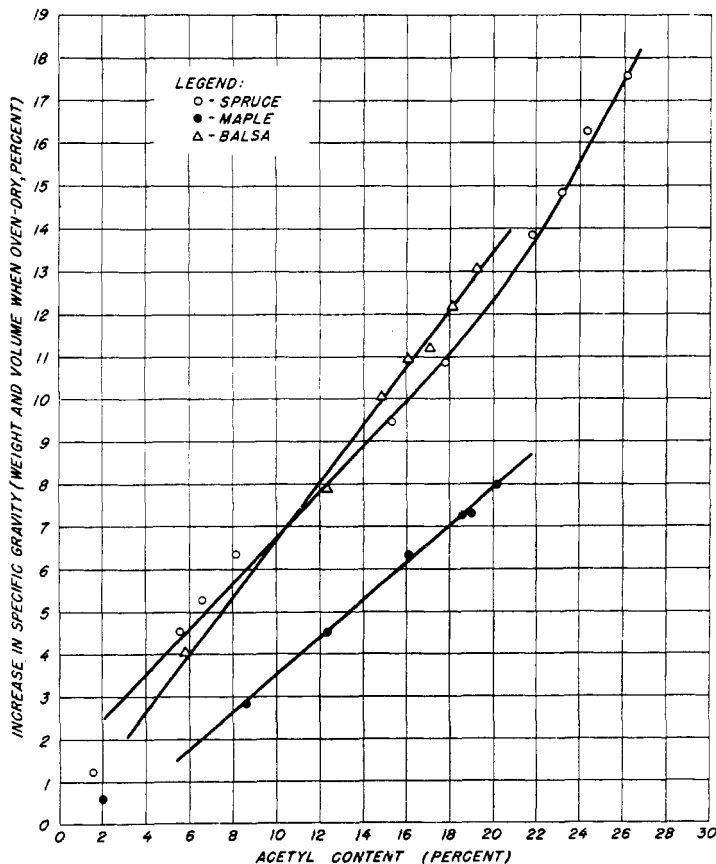

FIG. 3. Relationship between the acetyl content and the percentage increase in specific gravity.

percentage increases in specific gravity are less than those based on oven-dry weight and volume. At 65 per cent relative humidity, for example, untreated spruce has a moisture content of 12 per cent, whereas spruce with an acetyl content of 20 per cent, having an antishrink efficiency of 60 per cent and a reduction in hygroscopicity of 50 per cent, has a moisture content of 6 per cent. Under

these conditions, the increase in specific gravity at test over that of untreated wood is 9 per cent rather than 12 per cent. Similarly, the specific gravity increase of maple at test (65 per cent relative humidity) is only 5 per cent, in contrast to 8 per cent for the dry wood.

The limited strength tests that have been made to date indicate that dry acetylated wood has practically the same strength properties as the untreated controls except in the case of toughness. The toughness is either unaffected or is increased by as much as 20 per cent. The strength properties in equilibrium with high relative humidities should, in general, be improved because of the lower moisture content of the acetylated material.

Mechanism of stabilization

Table 2 gives data to show that the dimensional stabilization of wood attained by acetylation is primarily due to a bulking effect. Although acetylation appreciably increases the oven-dry dimensions of wood, originally having the same

TABLE 2

Volumetric changes in the system acetylated spruce–water

PROPERTY	UNTREATED WOOD	ACETYLATED WOOD
Oven-dry volume of spruce before acetylation, cc........	5.71	5.73
Subsequent acetyl content, per cent by weight..........	0.00	28.6
Oven-dry volume after acetylation, cc..................	5.71	6.23
Water-swollen volume, cc.............................	6.45	6.47
Volume change on immersion in water, cc..............	0.74	0.24
Antishrink efficiency, per cent.......................	0	70
Total volume change (acetyl and water), cc............	0.74	0.74

dry untreated volume, the water-swollen dimensions of the untreated and the acetylated wood are practically identical.

It may be argued that the replacement of the hydroxyl groups by the acetyl groups causes the stabilization as a result of the replacement of hydrophilic groups by less hydrophilic groups. Evidence, however, has been accumulated which suggests that the reduced polarity is not so probable a cause of stabilization as the bulking effect. Wood was acetylated, propionylated, and butyrylated. If stabilization resulted from the replacement of hydroxyl groups by the acyl group (acetyl, propionyl, or butyryl) for a given acyl content, the acetylated wood should have the greatest antishrink efficiency, the butyrylated wood should have the lowest, and that of the propionylated wood should lie between that of the acetylated wood and the butyrylated wood. This would be so because of the increasing molecular size and, therefore, because of the decreasing number of hydroxyl groups replaced as the molecular size of the acyl group increases.

Actually, all three treated specimens have the same antishrink efficiency. Yet only two-thirds of the hydroxyl groups replaced in acetylated wood are replaced in butyrylated wood. Thus it seems that the extent of stabilization obtained by acylating wood depends primarily on the bulk of the acyl groups

laid down per unit weight of wood. The single curve of figure 4 in which the volume of the acyl groups (acetyl, propionyl, or butyryl) per unit weight of wood is plotted against the antishrink efficiency holds for acetylated, propionylated, and butyrylated wood. The calculated specific volume of the acetyl group, the
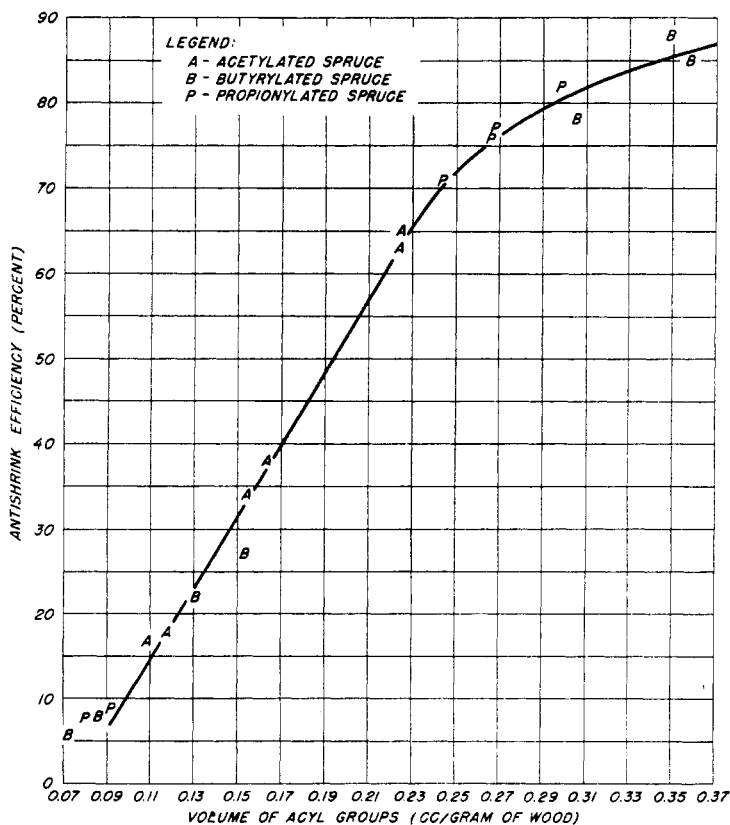

FIG. 4. Relationship between volume of acyl groups per gram of wood and the antishrink efficiency.

propionyl group, and the butyryl group used in the calculations is 0.902, 1.00, and 1.055 cc. per gram, respectively.

The bulking effect expressed as the increase in oven-dry volume caused by acetylation is, in general, equal to the volume of the acetyl groups. This is shown in figure 5, in which the volume of the acetyl groups per gram of wood is plotted against the external volumetric swelling of the wood. The volume of the

acetyl groups was obtained by multiplying their weights by their calculated specific volume. The slope of the curves for spruce and maple is unity, as is the case for normal woods swelling in water, the volume of liquid taken up adding its volume to that of the cell wall and the fiber cavities changing an insignificant
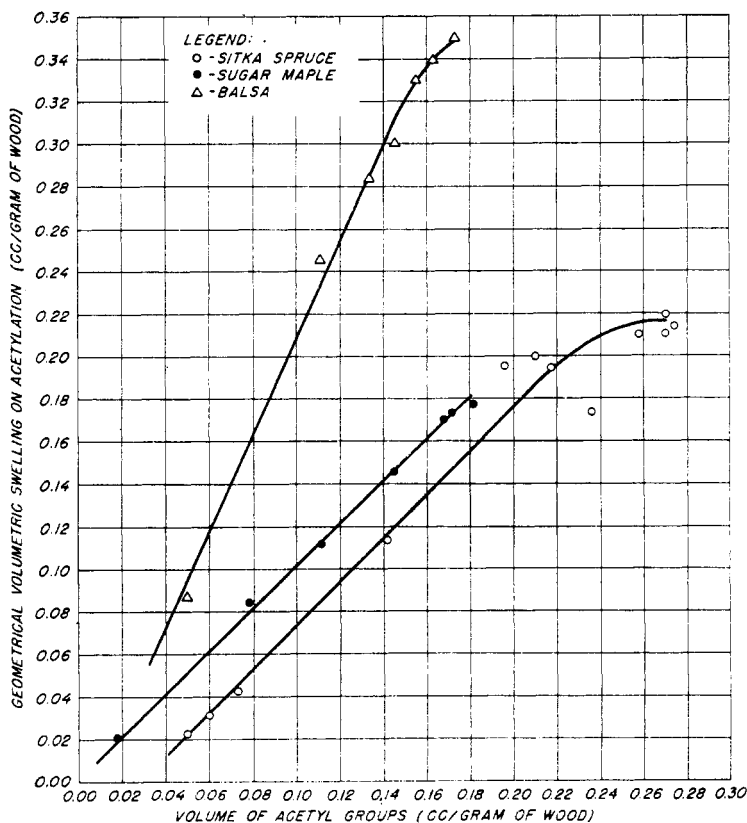

FIG. 5. Relationship between the volume of the acetyl groups and the external volumetric swelling.

amount in size (15). Balsa is abnormal in that the slope of the curve is about 2; that is, the increase in external volume is about twice the volume of acetyl groups taken up. Swelling of balsa in water is similarly abnormal. Swelling of balsa must be accompanied by an increase in the volume of the fiber cavities.

These data all indicate that the dimensional stabilization imparted to wood is due to a bulking effect which reduces the shrinkage. The fact that the acetyl

groups become chemically bonded to the wood throughout the cell-wall structure rather than merely being mechanically deposited within the cell wall apparently is of little importance in imparting dimensional stability to the wood. It may, however, be of considerable importance from the standpoint of permanence.

Harrison (3) has recently reported the hygroscopicity of partially acetylated, butyrylated, and stearoylated pulps. On comparing the hygroscopicity of such acylated pulps in which the same percentage of hydroxyl groups had been replaced, he finds a pronounced reduction in hygroscopicity as the size of the acyl group increases. Harrison believes this is due to an increasing hydrophobic character of the acyl group with increasing size.

Another explanation is offered, based on the bulking action of the acyl groups. It is assumed that the reduction in hygroscopicity of partially acylated pulp is equal to the volume of the acyl group laid down in the cell walls of the pulp. In other words, the total swelling that cellulose undergoes on partial acylation plus subsequent water gain remains constant regardless of the nature of the acyl group and regardless of the acyl content, provided this content is below such an

TABLE 3

Reduction in hygroscopicity of pulp on acylation

ACYL GROUP	ACYL CONTENT	VOLUME OF ACYL GROUP	HYDROXYLS REPLACED	REDUCTION IN HYGROSCOPICITY
	weight per cent of pulp	*cc. per 100 g. pulp*	*per cent of total number*	*per cent*
Acetyl...............................	22.3	20.1	28.0	25
Butyryl..............................	16.3	17.2	12.4	25
Stearoyl.............................	17.3	19.5	3.5	25

amount where no disruption or polymorphic change (5) in the cellulose can occur. Table 3 has been constructed from Harrison's data.

It will be noted that all acylated pulps have the same hygroscopicity, even though 28 per cent of the total number of hydroxyl groups are replaced by acetyl groups, 12.4 per cent replaced by butyryl groups, and only 3.5 per cent replaced by stearoyl groups. On the other hand, it will be noted that the *volume* of the acyl groups laid down in the pulp seems to be approximately the same. Thus the hygroscopicity of partially acylated pulp seems to be governed primarily by the volume of the acyl group laid down rather than by the number of hydroxyl groups which have been replaced. It should be emphasized that this relationship holds only providing the volume of the acyl group is not sufficient to change the polymorphic configuration of the cellulose unit cell. For greater acyl contents, the assumption no longer holds that the total swelling on acylation and moisture gain remains constant. At these higher acyl contents, volumetric changes in the size of the unit cell of cellulose complicate the calculations.

CONCLUSIONS

It has been shown that wood can be acetylated by a vapor-phase treatment with acetic anhydride and pyridine so as to avoid breakdown of the wood struc-

ture.   This treatment gives the highest degree of dimensional stabilization on a moisture equilibrium basis thus far obtained.   The resulting ester is quite stable. Unlike other dimension-stabilizing treatments, the wood is not embrittled.   It has other strength properties about the same as those of untreated wood.   It is highly resistant to decay, termites, and marine borers.   The dimensional stabilization is primarily due to a bulking effect by the acetyl groups, which causes an increase in the dry dimensions without increasing the wet dimensions.

REFERENCES

(1) BATESON, B. A.: Chem. Trade J. **105** (8) (2724), 93 (1939).
(2) BROWNE, F. L.: Ind. Eng. Chem. **25**, 835 (1933).
(3) HARRISON, J. J.: Paper Trade J. **119**, 28 (1944).
(4) HESS, K.: Ber. **61**, 1460 (1928).
(5) HESS, K., AND TROGUS, C.: Z. physik. Chem. **B15**, 157 (1932).
(6) HUNT, G. M.: U. S. Dept. Agr. Circ. **No. 128** (1930).
(7) MULLEN, J. W., AND PACSU, E.: J. Am. Chem. Soc. **63**, 1487 (1941).
(8) STAMM, A. J.: J. Am. Chem. Soc. **56**, 1195 (1934).
(9) STAMM, A. J.: U. S. patent 2,060,902 (November, 1936).
(10) STAMM, A. J.: U. S. patent 2,296,316 (September, 1942).
(11) STAMM, A. J.: Ind. Eng. Chem. **29**, 833 (1937).
(12) STAMM, A. J., BURR, H. K., AND KLINE, A. A.: Ind. Eng. Chem. **38**, 630 (1946).
(13) STAMM, A. J., AND HANSEN, L. A.: Ind. Eng. Chem. **27**, 1480 (1935).
(14) STAMM, A. J., AND HANSEN, L. A.: Ind. Eng. Chem. **29**, 831 (1937).
(15) STAMM, A. J., AND LOUGHBOROUGH, W. K.: Trans. Am. Soc. Mech. Engrs. **63**, 329 (1942).
(16) STAMM, A. J., AND SEBORG, R. M.: Ind. Eng. Chem. **31**, 897 (1939).
(17) STAMM, A. J., AND SEBORG, R. M.: Trans. Am. Inst. Chem. Engrs. **37**, 385 (1941).
(18) STAUDINGER, H.: Ann. **529**, 219 (1937).

KINETICS OF HOMOGENEOUS GASEOUS REACTIONS IN FLOW SYSTEMS

G. M. HARRIS

Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

INTRODUCTION

A review of the literature indicates that a number of special cases of the kinetics of flow systems have from time to time been the subject of theoretical treatment.   Recently, general discussions have been given by two authors (3, 6), but their concern was primarily with applications to large-scale industrial operations.   It is the purpose of the present paper to reëxamine and elaborate the theory of reactions in flow systems, with special regard to the requirements of experimenters in the field of the kinetics of homogeneous gaseous reactions.

Many years ago, both Bodenstein (2) and Langmuir (7) drew attention to the