Variable Retention of Water by Dry Wood

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Synopsis

When small wood (or cellulose) samples are vacuum-dried at room temperature, their final weight is found to vary according to their previous sorption history. The weight variations, of up to 1%, are shown to be due to strongly retained water. A minimum weight is obtained reproducibly ($\pm$ 0.01%) only when the wood is dried rapidly from the wetted state. When wood thus dried is exposed to water vapor and redried, water is retained even after drying for long periods or at higher temperatures (65°C.) and is removed only by again wetting and redrying the wood. The quantity of water retained is greatest after exposure to relative vapor pressures of approximately 0.5 and increases linearly with the square root of time of exposure up to at least 1000 hr. As some of these phenomena have been reported for the wool–water system also, it is possible that other polymers, particularly those which swell in water, may behave similarly. The significance of these results for the experimental determination of moisture content and the study of water sorption is discussed.

INTRODUCTION

At many points in the field of forest products technology and research, it is necessary to know the moisture content of wood and related materials. This moisture content is usually expressed as a fraction or percentage of the weight of dry wood and, for technical purposes, an accuracy of 0.5% moisture content may be sufficient.   On other occasions, however, the dry weight or moisture content may need to be known with the highest accuracy possible.   An analogous situation exists in the closely related field of textiles.

During more than 50 years of research, many methods for the determination of moisture content of these materials have been proposed, examined, and re-examined. Some of these methods are direct and determine the weight of water present using oven or vacuum drying.   Removal of water by Dean and Starke distillation or by chemical reaction with materials such as calcium carbide, acid chlorides, or the Karl Fischer reagent is also used. However, all of these methods are slow.   For more rapid but less accurate determinations, electrical methods, colorimetry, and hygrometry have been proposed, but these methods must be appropriately standardized against one of the direct methods.

Unfortunately, the different methods frequently yield different estimates of the water present.   In a recent contribution, for example, Kollmann and

Hockele[1] compared several different methods of drying wood and showed possible sources of error.   .

The method of drying most commonly used, at least for routine moisture content determinations, is oven drying at approximately 105°C. It is not very precise, however, for several reasons: (1) drying is not complete and residual moisture contents up to 1% may occur (due to doubt to the slight but variable ambient humidity in most laboratory ovens); (2) no precise endpoint to drying is reached, as prolonged drying leads to slow but continuous weight losses; (3) in wood, at least, irreversible changes occur, leading to darkening of color, embrittlement, and reduction in subsequent swelling properties.

For some types of investigation, e.g., sorption studies, it may be desirable not only to dry wood with maximum precision, but to be able to do it repeatedly on any one specimen and without affecting the subsequent sorptive behavior. Vacuum drying at room temperature or as little above it as possible appears best to meet these requirements. In vacuum drying cellulose, a temperature of 60–80°C. has been considered necessary by some workers, e.g., Lang and Mason.[2] Whether drying under these conditions is "complete" or merely reproducible remains to be established but Kollmann and Hockele[1] showed that wood vacuum-dried at room temperature contained moisture which could be detected by the Karl Fischer reagent. Clearly, only wood freed of other volatile contents can be used for sorption studies using vacuum drying.

It is well known that during the first drying from the naturally green condition, some irreversible changes occur in the sorptive properties of wood and other cellulosic substances which have never previously been dried out. Unless these changes are the primary object of study, it is common practice to cycle test materials between dry and nearly saturated conditions several times in order to stabilize them.[3,4] The dry weights and sorption isotherms then generally become reproducible. However, in our sorption studies of wood and related materials, it had been noticed that erratic changes in the dry weight of a sample sometimes occurred between successive vacuum dryings. These were small and apparently nonsystematic and were attributed either to loss of sample fragments, to gain of contaminating sorbate, e.g., traces of mercury vapor, or to errors of measurement. Most samples used in these studies had been stored for a period under ambient atmospheric conditions.

Attempts were made to improve the experimental precision. Greater care in preparation of the wood specimens (thin microtome sections) included washing in light petroleum and distilled water immediately prior to use. It was soon found that, following a sorption experiment of any considerable duration, e.g., a week or more, the dry weight of these samples invariably increased quite markedly. These changes were much greater than the probable errors of measurement and were attributed at first to contamination of the specimen. Precautions were therefore taken to eliminate possible contamination in turn from mercury vapor,

silicone pump oil, high vacuum lubricants, phosphorus pentoxide, and sulfuric acid spray or from the electrostatic pickup of dust particles and to avoid possible changes arising from photochemical reactions stimulated by ultraviolet light. In spite of these many precautions, similar increases in dry weight occurred whenever a fresh specimen was used.

Subsequent extraction of the sample in distilled water was then tried and although no likely contaminant could be detected in the rinsing water, the dry weight of the sample returned to its original value. It was soon confirmed that drying of a sample directly from the wet state yielded a minimum and reproducible dry weight. It was finally concluded that the increases in dry weight were due to small amounts of water retained by the wood in a manner resisting vacuum drying, except when this was conducted rapidly from a wetted condition.

Watt and Kennett[5] reported very similar phenomena in the sorption of water vapor by wool. They found that the amount of water retained was dependent on the length of previous exposure to water vapor and also on the relative vapor pressure during this exposure, a maximum retention occurring at approximately 0.5 relative vapor pressure. In the case of wool, the retained water could be removed by exposing the wool to saturated water vapor before vacuum drying. Subsequently Rounsley[6] found a similar retention of water by paper but no detailed study was made.

Explanations of the phenomena described by Watt and Kennett were understandably sought by them in terms of the properties of wool. If similar phenomena occur in wood, cellulose, and perhaps other polymers as well, it is clear that a more general interpretation is needed. This paper is therefore concerned firstly with presenting the evidence of water retention by wood at the end of vacuum drying and of its easy removal after wetting the wood. Secondly, the possible factors affecting its retention are examined and where possible compared with the observation on wool. Finally an attempt is made to assess the significance of the results from the points of view of possible mechanism, routine determination of moisture content, and research into problems of sorption involving the determination of the true dry weight of wood and similar materials.

DEFINITIONS

In the following description, some terms are used in a special sense. To avoid ambiguity these are defined as follows.

Rapid drying consisted of evacuation at a temperature of 27°C., unless otherwise stated. The pressure around the speciman was reduced to less than 0.2 mm. Hg within a few seconds, and the pumping was continued as rapidly as possible. When the pressure fell to less than 0.002 mm. Hg, an evacuated phosphorus pentoxide trap was opened. Drying under vacuum with the P_2O_5 was continued for a minimum of 24 hr. or until constant weight was reached at pressure of 0.0001 mm.

Slow drying concerns any process of desorption via one or more equilibrium steps or, if in one step, at a rate much slower than the maximum rate

attainable under conditions of rapid drying (see above). It also was concluded by exposure to P_2O_5 under vacuum until a constant weight was reached.

Dry weight was the final constant weight reached after drying by either the rapid or slow methods at 27°C. unless otherwise stated. The dry weight differed according to the previous sorption history of the sample.

Reproducible minimum weight is defined as the final constant weight obtained by rapid drying from the wetted state.

Retained water content corresponds to the difference between the dry weight and the reproducible minimum weight expressed as a percentage of the latter. It represents water held by the wood even after prolonged evacuation, but released during rapid drying from the wetted state.

MATERIALS AND METHODS

Materials

Cellulose. A film of regenerated cellulose approximately 6.5 μ thick was prepared from Analar grade cellulose acetate by evaporating an acetone solution on a glass plate. After removal, the film was saponified with alcoholic potash then washed with anhydrous alcohol, aqueous alcohol and distilled water, until it was alkali free. The film was then air-dried and sliced into strips approximately 1 cm. wide and about 7 mg. of it was suspended from a fused quartz helix microbalance.

Wood. The species of wood used was klinki pine (*Araucaria klinkii* Lauterb.) which had been used for earlier sorption studies. Microtome sections 40 μ thick and 2 cm.^{2} in area were cut from the tangential face of a small block (i.e., in the plane of the growth rings). The sections were air-dried at 20°C., extracted three times with light petroleum (40–80°C.), then soaked in distilled water at 65°C. for 1 hr., during which time the water was changed twice. In commencing any experiment, the specimen was suspended wet from the quartz helix microbalance and dried rapidly to give its reproducible minimum weight, usually 7–10. mg.

Apparatus and Techniques

All moisture content measurements were made by using a quartz helix sorption balance. This had a sensitivity of approximately 10 mm./mg. and a load capacity, within the 1% linearity range, of 15 mg. Helix extensions were measured by a cathetometer reading to 0.01 mm. held at a constant temperature ±1°C.

The sorption balance was suspended in a smooth-walled glass tube connected via taps to a P_2O_5 drying flask, a manometer, water vapor sources, and vacuum pump. The vapor sources consisted of deaerated distilled water or deaerated magnetically stirred sulfuric acid solutions. The sorption tube, manometer, drying tube, and vapor sources were housed in an air thermostat held at 27 ± 0.02°C.

In order to be able to rewet a specimen during the course of investigation without removing it from the sorption tube, a sintered glass septum was placed horizontally in the tube a little distance below the suspended specimen.   The lower surface of the septum was connected by a glass tube and tap to a water reservoir outside the sorption tube.   To wet the specimen on the helix, water was admitted by adjusting the pressure difference between the water reservoir and sorption tube until the top surface of the spectrum was flooded.   The helix was then extended by a vacuum-tight lever until the specimen touched the water surface.   When wetting was complete most of the water was withdrawn from the septum, the remainder being evaporated during the subsequent drying of the sample.   If necessary, the sample could be detached from the septum by the lever.

The effect of vacuum drying at an elevated temperature (65–70°C.) was also studied.   For this, the sorption tube was surrounded by a radiant heater, consisting of a heavy gauge copper shield, blackened inside, and electrically heated by a cable element attached outside.   The temperature of the radiating surface was monitored by a thermocouple.   By wrapping a microtomed wood section around the bulb of a thermometer placed in the normal sample position in the evacuated sorption tube, the specimen temperature and thermocouple readings could be correlated in advance.   They differed by only a few degrees.

EXPERIMENTAL RESULTS

Evidence of Dry Weight Variation

There would be little point in presenting all the experimental evidence which led finally to the conclusion that the observed variations in dry weight were associated with retained water.   However, several of the results obtained during this stage of the investigations are of interest.   The first of these are shown in Table I and were determined from a freshly prepared film of regenerated cellulose of 6.5 μ thickness (comparable with that of two adjacent cell walls in wood).

TABLE I
Variation in Dry Weight of Regenerated Cellulose

Sequence of dry weight determinations	Sorption history since previous drying[a]	Increase in dry weight above initial value, %
1	Initial drying	0
2	→0.2→0.3→SVP→0	0.29
3	→Light petroleum→SVP→0	0.28
4	→0.71→0.83→SVP→0	0.34
5	→H₂O immersion→0	−0.03
6	→H₂O immersion→0	−0.03
7	→0.5→0	0.38
8	→SVP→0	0.23

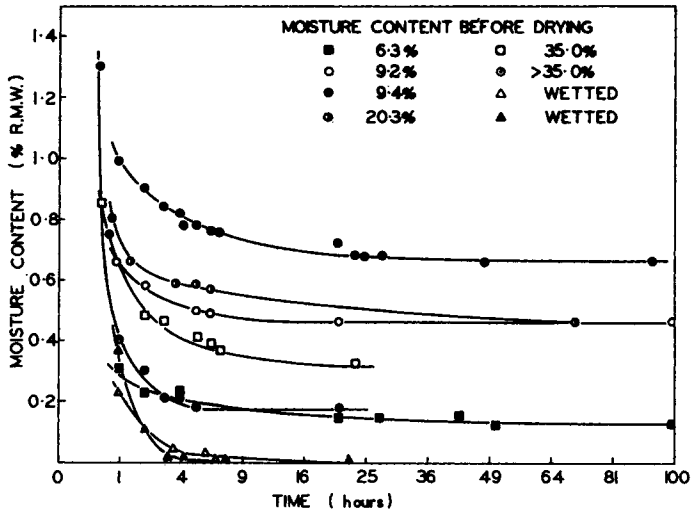[a] Figures are relative vapor pressure; SVP denoted saturated vapor pressure.

Fig. 1. Approach to different equilibrium water contents (retained water) during vacuum drying of wood samples at 27°C., the water retained depending on the previous sorption history.

The changes in dry weight after each of eight successive dryings are given, together with the intervening treatment or sorption history. Although the initial drying was from the air-dry state, the film had recently been wetted during its preparation.

From these results alone the following points may be seen to be illustrated.

(1) Dry weight changes occurred also in regenerated cellulose film (all other results to be presented were obtained using wood as test material).

(2) From drying sequences number 2 and 3, the increase could not be removed by extraction of the sample with light petroleum.

(3) Exposure to saturated vapor prior to vacuum drying did not return the sample to its original condition.

(4) A single immersion in water prior to drying was sufficient to release the retained water and enable slightly less than the original dry weight to be obtained. (Presumably, the original dry weight was a little high after exposure of the film to ambient humidity during the preliminary air drying and setting up.)

It might be supposed that the variations in dry weight were due to differences in the rates of drying and removable by prolonged drying. That this is not the case may be seen from Figure 1, where the final stages of drying are shown for a selection of wood samples. They were dried from different initial moisture contents and finished with different amounts of retained water (these two quantities not necessarily being related). Although samples dried from the wet state tended to reach their minimum weight more rapidly (in less than 10 hr.) than those having retained water

(over 10 hr.), there is no suggestion that prolonged drying would have removed this water.

Finally, to show that the effects observed were not in some unsuspected manner associated with the sorption apparatus and techniques in use, the change in dry weight was confirmed by using a larger sample and a direct weighing technique. A piece of air-dry klinki pine wood approximately 100 mm $\times$ 2 mm. $\times$ 1.5 mm. which had been stored under room conditions for several years was placed in a thin glass tube closed by a tap and weighed. After drying by evacuation at room temperature (20°C.) to constant weight, it was moistened and then redried under the same conditions. A dry weight lower by 1.05% was obtained.

Reproducibility of the Minimum Weight

That the dry weight obtained by rapidly drying a wetted specimen was in fact a reproducible minimum value was established from several experiments. The results from one of these are shown in Table II. The dry

TABLE II
Reproducibility of Dry Weight

Vacuum drying pretreatment[a]	Duration of moisture treatment, hr.	Vacuum dry moisture content, %
Rewet	$^1/_2$	0.00
0.47 RVP	43	0.14
Rewet	$^1/_2$	0.00
0.56 RVP	69.5	0.20
Rewet	$^1/_2$	0.00
0.65 RVP	43	0.14
Rewet	$^1/_2$	0.00

[a] The wood specimen received an initial pretreatment consisting of extraction with light petroleum for $^1/_2$ hr. and soaking in two changes of distilled water at 60°C. for 1 hr. before being placed in the sorption apparatus and rapidly dried. RVP denotes relative vapor pressure.

weight after the initial rapid drying from the wet state was taken as reference. After the initial drying, the sample was rewetted and redried to confirm that the minimum weight had been reached. It was then exposed to 0.47 relative vapor pressure for 43 hr. as shown and dried to constant weight. This was 0.14% above the initial value. After a further wetting and redrying, the original weight was again obtained exactly. Two further sequences of exposure to vapor, drying, wetting, and redrying each led to increases in dry weight and subsequent removal. It thus appears that the initial reference weight was in fact a minimum and reproducible value. It may be mentioned here also that no lower dry weight than that obtained by vacuum drying from the wet state at room temperature has been observed in these studies, except at the expense of permanent chemical or physical changes to the wood (see below for effect of temperature).

Factors Affecting the Quantity of Retained Water

Having established that the dry weight of wood and cellulose, as determined by vacuum drying, increases after exposure to water vapor, it was decided to study the phenomenon further. The following factors were selected as most likely to affect the variations in dry weight: (1) the relative vapor pressure to which the specimen is exposed prior to vacuum drying (RVP); (2) the length of time of exposure to water vapor atmosphere before drying; (3) the speed of drying, especially during early stages of drying (4) the temperature of drying.

With the exception of speed of drying, these factors were also investigated by Watt and Kennett and found to affect the variations in dry weight of wool.

Effect of Relative Vapor Pressure. A wood specimen at its reproducible minimum weight was exposed for approximately 20 hr. at 27°C. to water vapor at constant pressure and then rapidly dried to give a new dry weight which was recorded. It was then wetted and redried rapidly to its reproducible minimum weight. The cycle was repeated several times with progressively higher vapor pressures. The retained water contents after 20 hr. exposure to each of several vapor pressures was thus obtained. In a second similar experiment the period of each exposure to water vapor was extended to approximately 60 hr. Results are shown in Table III.

TABLE III
Effect of Relative Vapor Pressure on Retained Water Content of a 40 μ Wood Section
Initially at Minimum Dry Weight

Relative vapor pressure	Retained water content, %	
	20 hr. exposure	60 hr. exposure
0.09	0.02	0.03
0.20	0.05	0.05
0.31	0.04	0.12
0.44	0.08	0.23
0.54	0.18	—
0.59	0.12	0.21
0.67	0.11	0.16
0.76	0.11	0.25
0.90	0.11	0.17
Saturation	0.08	0.00

Examination of these results shows that, despite some scatter, the greatest retention of water occurred after exposure to water vapor at the intermediate pressures. Retention also increased with the length of exposure. Both of these observations are qualitatively in agreement with those of Watt and Kennett for wool.

Effect of Time of Exposure to Water Vapor. A similar specimen at its reproducible minimum weight was exposed to water vapor at approximately 0.45 relative vapor pressure for a short length of time. rapidly
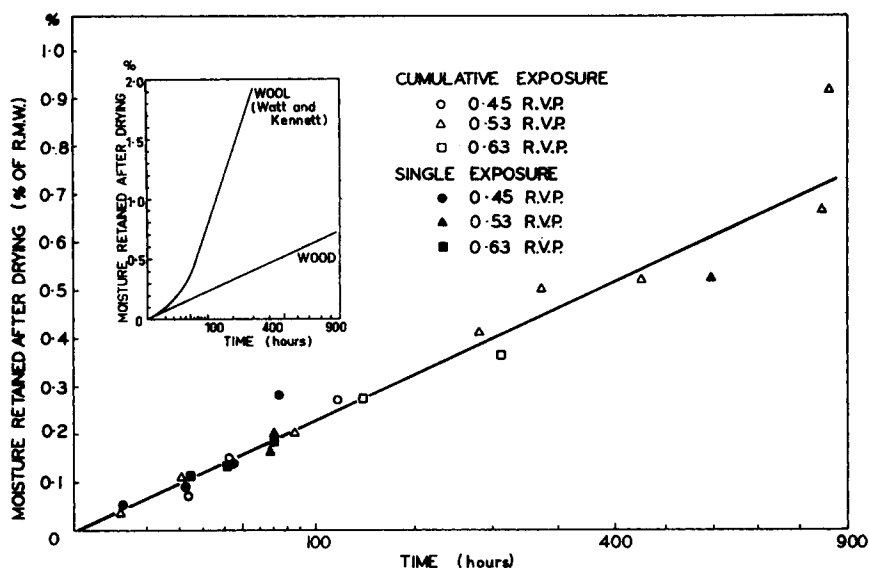
Fig. 2. Quantity of water retained after drying as a function of the total length of time of prior exposure to selected vapor pressures. The samples were initially at their reproducible minimum weight before exposure to vapor.

redried in vacuum without rewetting, and the new dry weight measured. It was then re-exposed to the same vapor pressure for a succession of further periods, the dry weight being determined after each without wetting. This experiment was repeated twice at relative vapor pressures of 0.53 and 0.63, respectively; the results are shown in Figure 2, where the retained water is plotted against the cumulative period of exposure but excluding periods during which the sample was drying or in the dry state.

The results show that changes in the wood-water system giving rise to water retention are relatively slow and were still going on at 970 hr., the longest time investigated. Figure 2 shows also that the increase in dry weight is very nearly a linear function of $t^{1/2}$. The comparatively small differences between the three vapor pressures arises from the fact that they were all near the vapor pressure for maximum effect (see Table III). At either high or low vapor pressures, smaller rates of increase in dry weight might therefore be expected.

Some differences between the wool–water and the wood–water systems appear when the data of Watt and Kennett for wool are similarly plotted (see inset in Fig. 2). For example, the initial portion of the wool–water data is distinctly curved. Also, the retained water content of wool can be as much as four times that found in wood after similar exposures.

One implication of a smooth relationship between the increase in retained water and the total time of exposure determined in the above manner is that intermediate drying of the wood between successive exposures to vapor merely stops any further increase in retention. On re-

exposure to vapor, the increase resumes as if no interruption had occurred. Confirmation of this was obtained by comparing retention after a given period of exposure with retention after a succession of shorter exposures equal in total time to the previous period. This may be seen in Figure 2, where the points representing single increments from the minimum reproducible weight are seen to lie close to the line for the cumulative increments.

It might have been thought that, if water retention was dependent on molecular rearrangements within the sorbent, fluctuations in moisture content and the accompanying swelling and shrinking could assist such rearrangements. No such effect appeared as a result of intermediate dryings (above), and this was confirmed in a separate test. In this the water retention after exposure to a fluctuating vapor pressure was found to be the same as that produced in the same time by the mean vapor pressure maintained steadily.

A further observation concerns the behavior of wood already containing considerable retained water when it is exposed to a low vapor pressure. It has been shown previously that at low vapor pressure the increase in retained water is very small or negligible. One question arising is whether the low retention is due merely to slowing down of the changes producing retention or whether large retentions already obtained are reduced when wood is subsequently exposed to low vapor pressures. To answer this, a dried sample containing 0.50% retained water was exposed for 24 hr. to a relative vapor pressure of 0.05 (an increase in equilibrium moisture content of ~2.5%) and then redried. It returned exactly to its previous dry weight. The test was then repeated with approximately 90 hr. exposure to a similar vapor pressure and also 24 hr. exposure to 0.20 relative vapor pressure, again with no change in dry weight after drying from either. On rewetting and rapidly drying the same sample, however, it came back exactly to its reproducible minimum weight as would be expected. Thus, at these low relative vapor pressures, there was no evidence of reversal of the changes leading to a retained water content of 0.50%. Also, the changing of the equilibrium moisture content, which is known to produce transient alterations to the mechanical properties of wood, did not affect the quantity of retained water. Similar negative results were obtained for experiments conducted at high relative vapor pressures (up to 0.90), and a retained water content of 0.92%.

Effect of Speed of Drying. The retention of water has so far been demonstrated to occur following adsorption processes only, i.e., after exposure to water vapor commencing from the dry state. The next step was to see whether similar retentions occurred following exposure to vapor commencing from the wet state, i.e., following a pause during the drying of a wetted sample. (In rapid drying, most of the water is removed during the first hour, which is considerably shorter than the exposure times required to produce measurable retentions.) The water vapor pressure around a wetted microtomed section was slowly reduced to 0.43 relative

vapor pressure over a period of 2 hr. The specimen was held at this pressure for 21 hr., then dried in a vacuum to a constant weight which represented a retained water content of 0.04%. In a further experiment the wetted microtomed section was dried through five approximately equal equilibrium steps over a total period of 168 hr., when it was found to have a retained water content of 0.15%. Although both these increases may be less than those expected following adsorption for similar times, it is clear that retention of water follows prolonged exposure to water vapor irrespective of whether the material is initially wet or dry.

Effect of Drying Temperature. In their work on wool, Watt and Kennett investigated the effect of raising the temperature during exposure to water vapor on the quantity of water subsequently retained after drying at room temperature and also the effect of raising the temperature during drying. They found that as the exposure temperature was increased to 65°C., the amount of water retained decreased slightly. Between 65 and 100°C., the amount of water retained was less the higher the exposure temperature, but it did not fall to zero. In the present experiments the effect of raising the temperature during drying only was investigated, that is, as a factor in removing the retained water already incorporated at 27°C. The drying temperature was approximately 65°C., there being some risk of chemical change in the wood above this temperature. Also this temperature is frequently advocated as desirable in the vacuum drying of cellulose. Drying was commenced at different initial moisture contents, the samples also holding different amounts of retained water.

In the first two tests (see Table IV), samples already dried at room tem-

TABLE IV
Effect of Drying Temperature on Final Retained Water Content

	Initial total moisture content, %	Drying time at 65°C., hr.	Final retained water content, %
1	0.21 (dried at 27°C.)	4	0.16
2	0.32 (dried at 27°C.)	4	0.29
3	10.9	5	0.12
4	30 (approximately)	4	0.15
5	wetted	4	−0.02
6	0.66 (dried at 27°C.)	91	0.26[a]

[a] Apparent value only owing to other changes in sample (see text).

perature but containing retained water were used, and decreases in weight after drying at 65°C. for 4 hr. were determined. It was necessary to cool the apparatus to 27°C. again before measuring the weights so that it was not practicable to determine the progress of weight changes during the short heating time.

From the first four results in Table IV, it will be seen that drying a wood section containing retained water at 65°C. did not restore it to its minimum reproducible weight. However, drying a wetted wood section for 4 hr.

at 65°C. (line 5, Table IV) yielded a dry weight only very slightly less than the reproducible minimum weight. The difference, if real, could well be the result of chemical changes in the wood even at this temperature (see below).

To confirm that a constant weight could be reached by vacuum drying at 65°C., a wood section containing 0.66% retained water was dried for 91 hr., but the heating was interrupted briefly at 24, 48, and 66 hr. to permit measurements. The data for the 91-hr. drying are presented in Figure 3 also. where it will be seen that a constant weight, still in excess of the reproducible minimum, was reached in 48 hr. (curve a) and that no further decrease in weight appeared likely. However, following the 91-hr. drying at 65°C., the wood section was rewetted and redried rapidly at
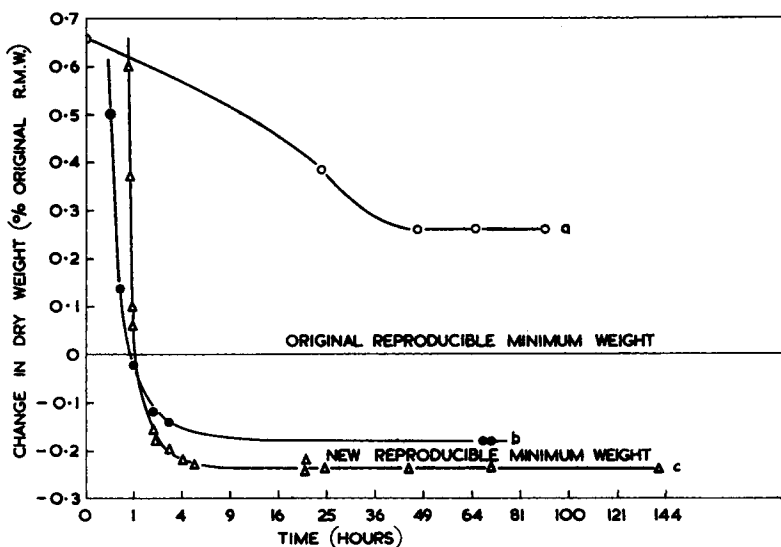

Fig. 3. (a) Reduction in weight of a dried sample containing 0.66% retained water on raising drying temperature from 27 to 65°C. (b, c) Change in reproducible minimum weight following subsequent wettings and dryings at 27°C.

27°C., when it was found that a new dry weight, 0.18% less than the previous reproducible minimum was obtained (curve b). A further rewetting and drying gave a dry weight 0.24% less than the reproducible minimum, but this was not further altered by subsequent rewetting and drying (curve c). This evidence suggests that some permanent change in the wood substance occurred during the long heating and that some of the degradation products were extractable with water. It is also possible that the first loss during the drying at 65°C. may have included decomposition products as well as some of the retained water.

It is of interest to note that Watt and Kennett obtained decreases in the dry weight of wool following heating at 100°C. in water vapor at 0.5 relative vapor pressure and during subsequent drying from saturated vapor

pressure in vacuum. They attributed this to degradation, and in their case the loss in weight occurred without water extraction.

Retained Water and the Kinetics of Sorption

One further observation remains to be reported. This concerns the dependence of the rate of sorption and swelling of wood on whether or not it contains retained water at the start of the sorption process. Details of these experiments will not be presented but the main conclusions are outlined.

From previous studies,[7] it has been found that when a wood specimen, which has been stored for a long time at ambient vapor pressure conditions, is vacuum-dried (thus retaining approximately 1% water), and is then exposed to a steady vapor pressure, the course of sorption of water vapor to the final equilibrium moisture content is complete within 24 hr. More recent measurements have shown, however, that when a specimen was first wetted and then dried to its minimum reproducible weight, the course of the subsequent sorption of vapor was different in two ways. Firstly, the main part of the moisture uptake was a little faster. Secondly, true equilibrium was not reached in 24 hr., but instead the moisture content showed a slow upward drift at a rate corresponding approximately with the rate of increase in retained water shown in Figure 2.

It has also been noted, during measurements of the rate of swelling of dry wood cell walls following rapid immersion in water, that samples containing retained water swelled less rapidly than samples initially dried from the wetted state.

GENERAL DISCUSSION

Before proceeding to a general discussion, the main features of the foregoing results may be outlined as follows.

(1) When wood is vacuum-dried at room temperature, a small amount of water (up to 1%) may be retained, even after prolonged drying.

(2) Increasing the temperature during drying decreases only slightly the quantity of water retained.

(3) A minimum dry weight is obtained reproducibly if the sample is first wetted by immersion in water and then dried rapidly at room temperature.

(4) Otherwise, the quantity of water retained on drying varies with the previous sorption history of the sample.

(5) The amount of water retained depends on the vapor pressures or moisture contents at which the wood has been held prior to drying. The maximum retention follows exposures at 0.4 to 0.6 relative vapor pressure.

(6) The retained water increases with the period of prior exposure to water vapor up to at least 1000 hr. The increase in retained water is approximately linear with root time over this period, and the exposure period need not be continuous.

(7) Retention of water occurs whether the conditioning moisture content is approached by adsorption or desorption.

In attempting to propose a mechanism that is consistent with all these phenomena, the close similarity between these results and those obtained on wool must be considered. From the results of Watt and Kennett, it may be seen that, with minor differences, all seven of the preceding statements are true of wool also.

It is thus clear that remarkably similar processes occur in both wood and wool. It has also been established as likely that regenerated cellulose film behaves similarly and there is reason to believe from a re-examination of earlier sorption data[7] that isolated lignin may do likewise. It seems, therefore, that an explanation of the phenomena should be sought in terms of properties of these polymer–water systems that are common to all of them, such as swelling, sorption hysteresis, hydrogen bonding, etc. Conversely, properties which are exclusive to a particular polymer, such as its morphological structure, distinctive reactive groups, etc., may be eliminated as a prime cause of the phenomenon.

While it is easy to agree with Watt and Kennett that the two most likely alternative explanations would be either high-energy bonding or physical occlusion, the total experimental data now available seem to cast doubt on both these mechanisms. Thus, on the one hand there is evidence of interaction between the retained water and the sorbent which, implying greater stability, tends to favor the explanation based on high-energy bonding. By high-energy bonding here is meant sorption of water by hydrogen bonding on sites of especially favorable configuration such that the maximum reduction in energy is obtained. This would merely represent a shift in the total spectrum of bond energies associated normally with sorption of water by these materials but not a marked change in the manner by which water is held. The evidence of greater stability lies in the change in mechanical properties reported for wool and the slower rates of sorption and swelling in water vapor and liquid, respectively, of wood containing retained water. Passive occlusion such as is known to occur with larger nonpolar molecules, e.g., benzene, does not seem so readily compatible with such changes in properties.

On the other hand, once water has entered the state of retained water, it behaves in many respects as if it were no longer part of the sorbate system at all but rather as an irreversible addition to the sorbent. Its presence in a sample might not even be detected during sorption experiments, if the sample were not at some stage subjected to saturating conditions followed by rapid drying. This behavior is more akin to some form of trapping than to sorption. Further, the very slow rate of incorporation of retained water, its high resistance to removal at elevated temperatures, coupled with its easy elimination at room temperature after wetting, taken together, do not seem consistent with simple high energy bonding.

In either of these mechanisms, it might be expected that the slow changes would involve, and might well be controlled by, rearrangement of molecules

or segments of the large molecules comprising wool and wood constituents. However, conditions conducive to such rearrangements, namely drying and re-exposure to vapor, have been shown not to accelerate the retention. Sepall and Mason,[8] on the other hand, showed that repeated moisture content cycling with deuterated water can lead ultimately to deuteration of all hydroxyl groups in cellulose, including those in initially inaccessible crystalline regions. Further, they found that this deuteration was most effective at either high or low moisture contents; by contrast, the changes leading to water retention proceeded most rapidly at intermediate humidities.

If neither high-energy bonding nor occlusion are accepted as the likely mechanisms, a satisfactory alternative is difficult to find. It becomes necessary to consider less likely hypotheses such as hitherto unrecognized changes in the state of aggregation of the adsorbed water. Such a conjecture has little merit at this stage, except to emphasize the possible importance of the common sorbate, water, rather than the divergent sorbents which are involved.

Significance for Moisture Content Determination

The results of this investigation have obvious implications for the experimental determination of moisture content. This has been a subject of discussion and research for many years without complete agreement. The present results suggest that variable retained water content is one possible source of ambiguity. The minimum reproducible weight is reached readily by vacuum drying at room temperature from the wet state but not after exposure of the material to water vapor for more than a few hours. The starting condition of materials used in previous drying studies may therefore have had considerable bearing on the results obtained. The resistance to drying after exposure to vapor accounts, at least partly, for the recommending of higher temperatures (65–80°C.) for the vacuum drying of cellulose. However, elevation of the drying temperature only partly reduces the retained water content and also introduces the possibility of other, more permanent, changes.

Whether or not the minimum reproducible weight obtained in these experiments represents the absolutely dry state has not been specifically determined nor whether it coincides with drying by the Dean and Starke method. This partly depends on the definition of the "dry" state. Generally, drying is meant to imply the removal of all water held primarily by physical (adsorption) forces up to and including hydrogen bonding, as distinct from that chemically bound. In practice, the distinction may not be so completely clear-cut. The present results suggest, however, that the minimum reproducible weight does, at any rate, represent a condition where a sharp transition in binding mechanism occurs. Firstly, there is its precise reproducibility at room temperature. Second is the fact that raising the drying temperature of wetted wood does not lower the minimum reproducible weight significantly, that is, the reproducible minimum weight

does not appear to be a variable equilibrium between moisture content and the drying potential. Thirdly, it was shown that prolonged drying from the vapor-exposed state at an elevated temperature does not yield a final weight lower than the minimum reproducible value.

The implication from these statements is that for accurate determinations of dry weight or moisture content when a drying procedure is used, it may be preferable to commence drying from the wet state, even if this must be produced artificially first. There are, however, obvious cases where this will not be desirable, e.g., where there is partial solubility of the sorbent or its constituents.

An additional problem now introduced, however, lies in deciding what moisture content it is in fact desired to determine. Evidence has been given that after prolonged exposure to water vapor some moisture is retained irreversibly in the material, contributing to its weight and structure in such a way as to at least appear to be an integral part of the sorbent. In many practical situations, the presence of this retained water would represent a more normal and certainly commoner state of the sorbent than that containing no retained water. The inclusion of retained water in an experimentally determined moisture content may thus be inappropriate for some purposes. It may not be possible to decide this until it has been established whether changes in, say, physical properties, are a function of total moisture content or only of the reversibly adsorbed water.

A further problem then raised by this consideration is that it may not be possible to distinguish sharply between water in the retained and the easily removed states, that is, the amount of retained water left in the sample will depend on the drying conditions, particularly the drying temperature.

The above considerations apply also to determining the moisture content or dry weight of a sample to be used for, say sorption studies. If drying is carried out in the manner necessary to yield the minimum dry weight, it must be recognized that subsequent sorption experiments, unless completed rapidly, will be affected by the slow changes, other than the reversible sorption process. If such changes are to be avoided, then use of material already containing retained water, that is, material which has been exposed for a considerable period to water vapor, would be preferable. Such material if dried in a carefully reproducible manner, should yield a reproducible dry weight. However, it will be necessary to know whether changes in the quantity of retained water may occur as a result of any other physical processes to which a sample under study may be subjected.

A close analogy would be the problem of drying a material capable of forming a relatively stable hydrate and of deciding whether one is concerned with studying the physical effects of water absorbed on the pre-existing hydrate or studying a process which includes the rehydration of the anhydrous material. Clearly the reference "dry weight" would be different in each instance.

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Résumé

Lorsque des petits échantillons de bois (ou de cellulose) sont séchés sous-vide à température de chambre, on trouve que leur poids final varie suivant leur historique de sorption antérieure. Les variations de poids, allant jusqu'à 1%, sont dues à la forte rétention d'eau. On peut obtenir un minimum de poids reproductible ($\pm 0.01\%$) uniquement lorsque le bois est séché rapidement à partir de l'état mouillé. Lorsque le bois ainsi séché est exposé à la vapeur d'eau puis reséché, l'eau est retenue, même après de longues périodes de séchage ou à des températures plus élevées (65°C) et est enlevée uniquement en mouillant de nouveau et en reséchant le bois. La quantité d'eau retenue est plus grande après une exposition à des pressions relatives de vapeur d'environ 0.5 et augmente d'une façon linéaire suivant la racine carrée de la durée d'exposition jusqu'au moins 1.000 heures. Comme certains de ces phénomènes ont également été décrits pour le système laine–eau, il est possible que d'autres polymères, particulièrement ceux qui gonflent dans l'eau, se comportent de la même façon. On discute de la signification de ces résultats pour la détermination expérimentale de la teneur en eau et pour l'étude de la sorption d'eau.

Zusammenfassung

Bei der Vakuumtrocknung bei Raumtemperatur von kleinen Holz- (oder Zellulose) proben erweist sich das Endgewicht als abhängig von der Sorptionsvorgeschichte. Die Gewichtsänderungen von bis zu 1% scheinen durch fest zurückgehaltenes Wasser bedingt zn sein. Ein reproduzierbares ($\pm 0,01\%$) Mindestgewicht wird nur bei rascher Trocknung des Holzes aus dem feuchten Zustand erhalten. Wenn ein derartig getrocknetes Holz mit Wasserdampf in Berührung gebracht und wieder getrocknet wird, so wird Wasser sogar nach Trocknung über lange Zeiten oder bei höheren Temperaturen (65°C) festgehalten und nur nach wiederholter Befeuchtung und Trocknung des Holzes entfernt. Die zurückgehaltene Wassermenge ist nach Einwirkung relativer Dampfdrucke von etwa 0,5 am grössten und nimmt linear mit der Quadratwurzel der Einwirkungsdauer bis zu mindestens 1000 Stunden zu. Da ähnliche Erscheinungen auch schon für das Wolle–Wassersystem mitgeteilt wurden, ist es möglich, dass sich andere Polymere, besonders solche, die in Wasser quellen, ähnlich verhalten. Die Bedeutung dieser Ergebnisse für die experimentelle Bestimmung des Feuchtigkeitsgehaltes und für die Untersuchung der Wassersorption wird diskutiert.