XCIV. THE BLEACHING ACTION OF ALKALINE HYDROGEN PEROXIDE ON WOOD

BY WILLIAM GEORGE CAMPBELL AND GEOFFREY SWANN

*From the Section of Wood Chemistry, Forest Products Research Laboratory,
Princes Risborough, Aylesbury, Bucks*

(Received 15 February 1938)

It is well known that in the presence of concentrated H_2O_2 and alkali wood undergoes vigorous decomposition at ordinary temperatures. At comparatively low concentrations, however, H_2O_2 has a bleaching action on wood which has found some application commercially. The mechanism of this bleaching action is little understood, and Schorger [1926, p. 385] has stated that the light colour obtained is seldom permanent. Marggraf [1917], who apparently first studied the action, obtained, in presence of NH_3 , satisfactory results with freshly felled maple, lime, aspen and white poplar woods. He observed that during the bleaching process the system rapidly became acidic. Grüss [1923] observed microscopically that after warming with concentrated H_2O_2 and subsequent drying the tracheids of pine wood became encrusted with crystalline material. Further, the treated tissue failed to give the so-called lignin colour reaction with phloroglucinol and HCl . König [1906, 1, 2] developed a method of estimating the cellulose content of forage grasses which was based upon the decomposition of lignin by means of H_2O_2 and NH_3 , apparently assuming that no decomposition of cellulose took place under the conditions of the determination. That isolated alkali-lignin can be partially converted into soluble products by H_2O_2 has been shown by Anderzen & Holmberg [1923]. The present series of experiments was undertaken in order to test the bleaching effect of H_2O_2 on a variety of woods and, in three specific instances, to examine the effect in terms of current analytical methods.

EXPERIMENTAL

Samples (2 g., air-dry) of each of the following woods in sawdust form were mixed with 25 ml. of a solution consisting of 4 parts H_2O_2 (20 vol. AnalaR), and 1 part 11.5 % aqueous NH_3 at room temperature (20°):

Douglas fir heartwood (*Pseudotsuga taxifolia* Brit.). Jarrah heartwood (*Eucalyptus marginata* Sm.). Gaboon ebony heartwood (*Diospyros? crassifolia*). Bog oak (*Quercus* sp.). Purpleheart (*Peltogyne porphyrocardia* Griseb.). Barwood (*Pterocarpus tinctorius* Welw.). Honduras rosewood (*Dalbergia stevensonii* Standl.). Andaman padauk (*Pterocarpus dalbergioides* Roxb.).

With the exception of purpleheart and ebony all of the samples were bleached to pale yellow or buff shades after 24 hr. The sample of purpleheart required 50 ml. of bleaching solution and 48 hr. to bring it to an ivory yellow shade, whilst the ebony required 75 ml. of solution and 72 hr. to produce a buff-coloured residue which was completely macerated and only represented a small proportion of the starting material. After thorough washing with cold water and drying *in vacuo* at $35\text{--}40^\circ$ none of the bleached woods darkened and no appreciable changes in colour have been observed to take place on subsequent exposure to air and light for 12 months. Drying of bleached wood at $100\text{--}105^\circ$ invariably caused darkening in colour which was more accentuated in some species than in others.

2 g. (air-dry) samples of each of the following woods in sawdust form were mixed with 25 ml. of a freshly prepared bleaching solution consisting of 5 parts H_2O_2 (20 vol. AnalaR) and 1 part 10 % NaOH at room temperature (20°):

Tasmanian oak (*Eucalyptus obliqua* L'Hérit.). Tasmanian oak or Alpine ash (*Eucalyptus delegatensis* R. T. Baker). Tasmanian oak or Australian oak (*Eucalyptus regnans* F. Muell.). Oak heartwood (*Quercus* sp.). Beech (*Fagus sylvatica* L.). Pine (*Pinus sylvestris* L.). Hard maple (*Acer saccharum* Marsh). Ash (*Fraxinus excelsior* L.).

After 24 hr. the samples of the three eucalypts as well as those of maple and ash had become bleached to a pure glistening white colour while the samples of the remaining species were bleached to a white colour with a faint yellowish tinge. In the case of *Eucalyptus obliqua* the concentration of NaOH (c. 2 %) could be reduced to 1 % provided that 40 ml. of bleaching solution were used for every 2 g. sawdust. The samples of bleached wood in all cases remained white provided that they were thoroughly washed with cold water and dried either at 40° *in vacuo* or by washing with 95 % alcohol followed by ether. Drying at 105° induced darkening to a pale yellow colour in each case. The surface layers of solid commercial samples of Tasmanian oak (*Eucalyptus* sp.) were bleached to a very light colour in approximately 1 hr. after being rubbed over in turn with H_2O_2 (10 vol.) and either dilute NaOH or NH_3 .

The effect of alkaline H_2O_2 on the chemical composition of wood

(1) *Douglas fir*. A 60 g. (air-dry) sample of 60–80 mesh Douglas fir wood flour was mixed with 600 ml. 20 vol. H_2O_2 and kept at 20° for 24 hr. after adding 120 ml. 11.7 % aqueous NH_3 . A 100 g. sample of the same material was treated for six successive periods of 48 hr. each as follows. For the first treatment the wood was mixed with 1 l. H_2O_2 and 100 ml. 11.7 % NH_3 . After 48 hr. the liquor was filtered off and for each subsequent treatment a further charge of 500 ml. H_2O_2 and 100 ml. NH_3 was added. After bleaching both samples were thoroughly washed with warm water until neutral to litmus, partially dried at 40° *in vacuo* and analysed (Table I).

Table I. *Analysis of 60–80 mesh Douglas fir and jarrah woods before and after bleaching with H_2O_2 and NH_3 at 20°*

(Results expressed as % by wt. of oven-dry original wood.)

	Douglas fir			Jarrah	
	Original wood	After bleaching for 24 hr.	After bleaching for 288 hr.	Original wood	After bleaching for 24 hr.
Loss in wt.	—	11.58	19.97	—	18.53
Cold water-soluble	3.48	0.19	0.67	0.49	0.58
Hot water-soluble	5.60	1.17	2.80	1.40	2.29
1 % NaOH-soluble	16.85	11.93	15.19	21.47	13.28
C. and B. cellulose	58.43	57.06	53.62	50.10	49.75
α -Cellulose	40.60	38.99	32.82	40.93	40.74
α -Cellulose as % of C. and B. cellulose	69.48	68.32	61.21	81.70	81.90
Lignin	26.94	22.29	17.79	36.98*	21.43*
Total pentosans	8.27	7.06	4.72	13.76	12.39
Pentosans in cellulose	3.18	2.81	2.08	5.86	5.73
Pentosans not in cellulose	5.09	4.25	2.64	7.90	6.66
Total methoxyl	4.48	3.77	2.92	7.13	5.55
Methoxyl in lignin	4.05	3.44	2.53	6.09	4.53
Total CO_2 on hydrolysis with 12 % HCl	0.605	0.67	0.492	1.032	0.985
CO_2 in cellulose on hydrolysis with 12 % HCl	0.362	0.28	0.229	0.422	0.405

* Uncorrected for "kino".

60 g. of 60–80 mesh, air-dry jarrah wood were treated under the same conditions for 24 hr. using 600 ml. 20 vol. H_2O_2 and 120 ml. 11.7 % NH_3 . The residue was analysed after washing and drying as above (Table I).

40 g. of 60–80 mesh, air-dry Tasmanian oak (*Eucalyptus obliqua*) mixed with 600 ml. 20 vol. H_2O_2 and 120 ml. of 10 % NaOH were well stirred and kept at 20° for 24 hr. The wood residue which had become pure white in colour was collected and washed in the usual way. Before analysis (Table II) excess water was removed by washing with alcohol followed by ether.

Table II. *Analysis of Tasmanian oak (Eucalyptus obliqua) before and after bleaching with H_2O_2 and NaOH for 24 hr. at 20°*

(Results expressed as % by wt. of original oven-dry wood.)

	Original wood	White residue after bleaching
Loss in wt.	—	23.96
Hot water-soluble	7.44	1.92
1 % NaOH-soluble	18.52	10.71
C. and B. cellulose	58.86	54.50
α -Cellulose	46.60	32.99
α -Cellulose as % of C. and B. cellulose	79.17	60.45
Lignin	19.57*	12.64*
Total pentosans	16.54	9.75
Pentosans in cellulose	9.33	6.51
Pentosans not in cellulose	7.21	3.24
Total methoxyl	6.62	4.46
Methoxyl in lignin	4.44	3.03
Total CO_2 on hydrolysis with 12 % HCl	0.815	0.870
CO_2 in cellulose on hydrolysis with 12 % HCl	0.590	0.427

* Uncorrected for "kino".

The action of alkaline hydrogen peroxide on isolated lignin

2.6144 g. of oven-dried (105°) beech lignin isolated by the method of Bamford & Campbell [1936] were finely powdered and mixed at room temperature with 200 ml. 20 vol. H_2O_2 and 20 ml. 2N NaOH. After 42 hr. a further 50 ml. H_2O_2 were added and after 90 hr. the dark brown solution was filtered on an alundum crucible of porosity RA 360. A small insoluble residue (0.0527 g.) was obtained after washing and drying at 105°. The addition of a slight excess of $BaCl_2$ to the clear, brown filtrate gave rise to a bulky buff-coloured precipitate which, after dehydrating in several changes of alcohol, centrifuging and drying *in vacuo* at 40°, was recovered as a pale brown powder which was not further investigated.

DISCUSSION OF RESULTS

The results show that, irrespective of whether they are in the seasoned or unseasoned condition, a wide range of woods can be bleached to permanent, light shades of colour by means of dilute alkaline H_2O_2 . Provided that the desired degree of bleaching can be obtained in a short period of time very little deterioration of wood substance is likely to take place, and dilute H_2O_2 and NH_3 , for example, should be suitable for bleaching the surfaces of veneers and speciality wood products. In most of the samples of sawdust examined bleaching was complete after 24 hr., but it has been shown that purely surface bleaching can take place in a much shorter period. Prolonged contact with the reagents merely leads to marked degradation of the major wood components without any improvement in bleaching effect. This is illustrated by the data in Table I. In the

case of Douglas fir, for instance, the loss in wt. incurred after bleaching for 24 hr. is largely accounted for by depletions of minor components and lignin. The loss of Cross and Bevan cellulose is slight, but its significance is confirmed by the results for α -cellulose, pentosans and CO_2 in the cellulose, all of which are slightly lower in the bleached wood. For most purposes this small amount of cellulose degradation is probably not serious. The remaining data for Douglas fir (Table I) show that, over a prolonged period, dilute H_2O_2 and NH_3 can cause extensive decomposition of all the major wood components at room temperature. The bleaching of the dark brown jarrah wood to cream colour was found to proceed smoothly. The data in Table I show that the loss in wt. in this case is largely made up of material derived from the apparent lignin. That this material is what is commonly referred to as "kino" is strongly suggested by the fact that a sample of exuded "kino" from a gum pocket in a jarrah tree [Campbell & Bryant, 1937] was transformed by H_2O_2 and NH_3 into soluble decomposition products of a pale straw colour. Under the conditions stated jarrah cellulose suffers little or no degradation during the bleaching process.

The most striking colour changes observed in the present study were those which occurred when NaOH was used as the activating agent for the H_2O_2 . The observation was first made on a sample of Tasmanian oak (*Eucalyptus obliqua*) in conjunction with Dr W. E. Cohen to whom grateful acknowledgement is here made. The bleached wood was pure white. It is shown above that similar results are obtainable with other hardwoods but a pure white product was not obtained from either of the softwoods examined. The data in Table II show that, in order to obtain a pure white residue, it is not necessary to remove all of the lignin from wood. The bleached wood gave a red chlorine:sodium sulphite colour reaction which was more pronounced than that given by the original wood. Further experiments are envisaged in which it is proposed to investigate more closely the properties of this white product. Apart from considerations of expense there are already indications that its production on a large scale from sawdust, groundwood etc., is unlikely to proceed as smoothly as its production under purely laboratory conditions, but further investigation of these latter questions could well be delayed until more fundamental information concerning the product itself is available.

The above experimental data go at least some way towards explaining the little understood mechanism of the bleaching action. The question naturally arises as to whether a dual role is played by the alkali in the system. It has been found [Forest Products Research Board, 1935] that the action of aqueous NH_3 in a wide range of concentrations on wood at room temperature is mainly confined to the solution of minor components with only slight decomposition of lignin and furfuraldehyde-yielding complexes and no decomposition of cellulose. Dilute NaOH at room temperature is known to be capable of removing hemicelluloses, some lignin and minor components from wood. In addition it probably induces slight decomposition of cellulose. Little or no bleaching action results from the contact of wood with dilute alkali alone. The immediate effect of adding either NH_3 or NaOH to wood is a pronounced darkening in colour. This is no doubt due in part to the extraction of certain components from the wood and in part to chemical reaction between those components and the alkali. There can be little doubt that although the most important function of the alkali is the liberation of energy from the H_2O_2 much must also depend on its solvent and swelling properties. In the bleaching process the order of events is usually as follows: (1) darkening of the wood followed by the leaching out of a dark-coloured extract, (2) simultaneous bleaching of wood and extract with

evolution of gas. In no case did the extract finally become colourless nor did the wood assume its palest shade of colour until after it had been thoroughly washed with water. Since the carbohydrates in wood are probably all white it must be assumed that bleaching of the wood as a whole is the result of leaching and chemical degradation of coloured minor components and/or lignin. It must be assumed that the non-carbohydrate components are decomposed by oxidation and that the products of the oxidation, either alone or in combination with alkali, are soluble in water. This view is strengthened by the knowledge [Anderzen & Holmberg, 1923] that lignin is decomposed to a mixture of carboxylic acids under conditions similar to those obtaining during the bleaching of wood.

It is a matter for comment that the apparent lignin which remains in certain woods after bleaching is colourless. This may be taken to indicate either that the original lignin present in such woods as Tasmanian oak, European beech, ash, oak etc., is colourless, or that in the course of the bleaching process lignin is oxidized in such a way that the groups which are responsible for colour are removed. In this connexion it was observed that the white residue from all the woods mentioned above only gave a very faint pink colour reaction with phloroglucinol:HCl in contrast to the deep magenta colour reactions of the original woods. The corresponding colour reactions given by the bleached softwoods examined were much more pronounced than those given by the bleached hardwoods. Without exception the lignin residues obtained in the analysis of the bleached woods were of the normal, chocolate brown colour. We are indebted to our colleague, Mr S. H. Clarke, for permission to state that microscopical examination of sections of Scots pine and ash woods which had been treated with 20 vol. H_2O_2 and NH_3 revealed that lignin had been removed from both middle lamella region and secondary walls. Further, it was concluded that the somewhat feeble colour reactions given by the secondary walls of bleached ash wood with chlor-zinc-iodine were an indication that the cellulose present in those walls was still masked by another substance.

If, during the bleaching processes referred to, conditions are sufficiently severe there is significant action on the wood cellulose. This is apparent from the results for Douglas fir (Table I) and Tasmanian oak (Table II) which indicate that the total effect is not merely confined to a small loss in Cross and Bevan cellulose. On the contrary it is much more insidious in that the % α -cellulose which can be recovered from the bleached woods are much lower than in the corresponding original woods. The full significance of these results will be discussed elsewhere but, in view of the uncertainty expressed by Heuser *et al.* [1924, p. 118] and by Schorger [1926, p. 270] concerning the action of H_2O_2 on cellulose, it should be mentioned that they are consistent with the view that the cellulose has undergone hydrolysis and not oxidation as might have been expected. This view is confirmed in part by the observation that the yield of CO_2 on hydrolysis of the Cross and Bevan cellulose is not enhanced as a result of the bleaching process, but chiefly by a previous observation made in this Laboratory [Campbell, 1937] that, under certain conditions, acid hydrolysis can produce the same effect on Cross and Bevan cellulose as has been observed here.

SUMMARY

1. It has been shown that a wide range of woods can be bleached to light shades of colour by H_2O_2 (20 vol.) in the presence of NH_3 or dilute NaOH at room temperature.

2. The residue remaining after treating certain hardwoods at room temperature with H_2O_2 (20 vol.) and 2 % NaOH is pure white although it retains a considerable amount of apparent lignin.

3. The colour of bleached wood is reasonably permanent provided that drying of the finished product is carried out at a low temperature (c. 40°).

4. The order of events in the bleaching process is (1) darkening of the wood followed by the leaching out of a dark-coloured extract and (2) simultaneous bleaching of extract and wood with evolution of gas.

5. It is suggested that certain non-carbohydrate components of the wood are leached out and decomposed by oxidation into products which, either alone or in combination with alkali, are soluble in water.

6. Under sufficiently severe conditions there is during bleaching some degradation of cellulose which is shown to be of a hydrolytic nature.

The authors are indebted to Mr W. A. Robertson, Director of Forest Products Research, for permission to communicate these results.

REFERENCES

- Anderzen & Holmberg (1923). *Ber. dtsh. chem. Ges.* **56**, 2044.
Bamford & Campbell (1936). *Biochem. J.* **30**, 419.
Campbell (1937). International Assoc. for Testing Materials. *Book of the London (1937) Congress*, p. 541.
— & Bryant (1937). *Biochem. J.* **31**, 748.
Forest Products Research Board (1935). *Annual Report*, p. 46. (H.M. Stationery Office.)
Grüss (1923). *Ber. dtsh. bot. Ges.* **41**, 53.
Heuser, West & Esselen (1924). *Textbook of Cellulose Chemistry*. (McGraw Hill, New York.)
König (1906, 1). *Ber. dtsh. chem. Ges.* **49**, 3564.
— (1906, 2). *Z. Untersuch. Nahr.- u. Genussm.* **12**, 387.
Marggraf (1917). *Kunststoffe*, **7**, 165.
Schorger (1926). *Chemistry of Cellulose and Wood*. (McGraw Hill, New York.)