LV. "FUMED" OAK AND NATURAL BROWN OAK.

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THE well-known process for the production of a brown coloration on oak by exposure to fumes from a solution of ammonia, or to ammonia produced by the decay of nitrogenous organic materials, appears to have been practised for a very long time. Apart from the fact that oak darkened by the action of ammonia is usually regarded as having an appearance superior to that of stained oak, the chief advantages of "fuming" oak are that the effect extends some slight distance below the surface of the wood, the grain of the wood is not raised, and uniform colouring is obtained in depressions and angles of woodwork, which is often not the case where stains are employed.

It is to be noted that in addition to the production of large quantities of "fumed" oak artificially, it is well known to those interested in timber that part of the wood of certain oak trees in this country is of a deep reddish brown shade. Usually the colour of this natural brown oak is much redder than the brown oak produced by the action of ammonia, and the grey appearance of the latter is usually absent from this natural brown oak.

It is apparently impossible to tell whether or not a given tree will contain any of this natural brown oak until it is felled. Although many of these "brown" oak trees are found in the neighbourhood of London, few people are aware of their existence [A. L. Howard, 1920].

It has been shown by P. Groom [1915] that the coloration of natural brown oak is due to the growth of a fungus, though very little appears to have been done with regard to this coloration from a purely chemical standpoint.

In view of the wide application of the "fuming" process for darkening oak and other woods, and the possibility of some connection between "fumed" oak and natural brown oak, it seemed advisable to carry out some experiments on the subject. The results so far obtained in this investigation are dealt with below.

The action of ammonia on oak in the presence and absence of oxygen.

It is usually stated that the brown coloration obtained on oak subjected to the fumes from a solution of ammonia is due to the action of the ammonia on the tannin contained in the wood. In view, however, of the fact that alkaline solutions of tannin absorb oxygen, it appeared at the outset that the

coloration obtained in the "fuming" process was most probably due to the combined action of ammonia and oxygen from the air. That this view is correct may easily be demonstrated as follows: small pieces of oak are introduced into test-tubes filled with ammonia gas standing over mercury. The ammonia is rapidly absorbed by the wood, but in the case of most samples of oak practically no change in the appearance of the wood is noted. In some cases where English oak is employed, however, a reddish brown coloration is produced, the depth of colour depending on the amount of ammonia absorbed. This reddish coloration is referred to later.

If instead of pure ammonia a mixture of ammonia and oxygen is used, on introducing the oak the gas is absorbed less rapidly, and at the end of the experiment the pieces of oak showed the ordinary coloration of "fumed" oak.

On exposing the pieces of oak which have absorbed only ammonia to the air the characteristic brown coloration of "fumed" oak is also obtained. If, however, shavings of English oak be placed in a flask which is then evacuated, or the air removed by hydrogen or coal gas, on the introduction of ammonia gas a reddish coloration is obtained on the oak. If the flask is then sealed this coloration may be preserved. It would appear, therefore, that both ammonia and oxygen are necessary for the production of the brown coloration.

The usual practice adopted in "fuming" oak on a large scale is to subject the wood to the action of ammonia escaping from a concentrated solution of the gas, access of air being possible throughout the whole operation.

The absorption of oxygen by oak in presence of ammonia.

In order further to investigate the absorption of oxygen by oak, a Hempel "phosphorus" pipette was filled with thin oak shavings, which were then covered with a dilute solution of ammonia—0.88 ammonia solution diluted 1 in 5 with water. The results obtained for various samples of oak are given in the tables which follow:

Volume of oxygen absorbed by 10 g. of oak shavings covered with a dilute solution of ammonia from 100 cc. of air in a given time.

(a) English and Japanese oak:

Time in minutes	5	15	60	—	Overnight
English oak	2.6 cc.	5 cc.	10 cc.	—	21 cc.
					(i.e. complete absorption of oxygen)
Japanese oak	3	7	10	—	21 cc.

At the end of the experiment the oak shavings were removed from the pipette, washed with water and dried. In both cases the shavings had the appearance of "fumed" oak, though not of a very deep colour.

(b) Heart wood and adjoining sap wood from same piece of English oak; and sap wood of American oak:

Time in minutes	5	15	60	240	Overnight
Heart wood	3.4 cc.	6 cc.	10 cc.	17 cc.	21 cc.
Sap wood (English)	0	0.4	1.8	4.2	9.4
Sap wood (American)	0	0	0	—	2.0

In the case of sap wood only a very faint "fuming" effect was observed at the end of the experiment.

It is well known to those engaged in the process of "fuming" that sap wood is not darkened to any marked extent by the action of ammonia. This is due to the fact that tannin is present in such small quantity in the sap wood.

It can be shown that no substance is present in the sap wood that inhibits the action of the ammonia, by soaking the sap wood in a solution of tannin, drying and subjecting to ammonia and air, when the ordinary "fuming" effect is produced.

(c) White and brown English oak from the same tree and "fumed" Japanese oak shavings.

Time in minutes	5	10	15	60
White oak	2.9 cc.	4.8 cc.	6.4 cc.	12.6 cc.
Brown oak	1.6	2.0	2.6	5.5
"Fumed" oak	0.0	0.0	0.2	1.2

After the experiment the brown oak had lost its reddish appearance and was more like ordinary "fumed" oak.

It will be noted that the absorption of oxygen is small in the case of the brown oak and that practically no absorption of oxygen took place with the fumed oak.

In other experiments instead of ammonia solution a solution of caustic potash was used as the confining liquid. With a 3 % solution of potassium hydroxide the absorption of oxygen was more rapid than when ammonia solution was used, but at the end of the experiment the oak after washing and drying did not show any appearance of "fumed" oak, nor was the effect produced on subjecting the oak after this treatment to the action of ammonia. It should be noted in this connection that sometimes a solution of potassium hydroxide is used for purposes of staining oak.

The potassium hydroxide solution in the "phosphorus" pipette at the end of the experiment like the ammonia solution was strongly coloured, but unlike the latter became considerably lighter in colour on keeping for some days. On the addition of hydrochloric acid to the dark coloured ammonia solution a dark brown precipitate was obtained, but in the case of the potassium hydroxide solution the precipitate was only very slightly coloured.

The amount of ammonia absorbed by oak during the fuming process.

In order to determine the amount of this ammonia, thin shavings of different kinds of oak were exposed for several days to the action of excess of ammonia and oxygen. A current of air was then drawn over the "fumed" wood for several hours after the smell of ammonia was no longer apparent.

Determinations of nitrogen by the Kjeldahl method in the oak before and after "fuming," and of the ammonia evolved on distillation of the "fumed" oak with sodium hydroxide, gave results as follows:

	N in "unfumed" oak. %	N in "fumed" oak. %	Calculated % of NH ₃ added	NH ₃ obtained on distillation with NaOH. %
Japanese oak	0.353	1.75	1.69	1.64
English oak	0.308	2.716	2.9	2.23

It will be seen that very much more ammonia was absorbed by the English oak, which was very dark in colour, after "fuming," than by the Japanese oak, which had a lighter brown colour. In the case of the Japanese oak practically the whole of the ammonia absorbed was evolved on distillation with sodium hydroxide, but with the English oak towards the end of the distillation the evolution of ammonia was extremely slow, and after several hours the amount of ammonia obtained was considerably less than that absorbed. From the results obtained in these experiments, and on the assumption that ammonia solution of 0.88 sp. gr. contains 35 % by weight of ammonia gas, approximately 8 g. of this solution would be required for complete "fuming" of 100 g. of shavings of this sample of English oak. For a similar weight of wood in one piece a very much smaller amount of the solution is, of course, required in actual practice where the fuming effect is confined to the surface of the wood.

It was found that practically the whole of the ammonia absorbed by shavings of Japanese oak could be recovered by prolonged extraction of the wood with hot water, although after extraction for several weeks the shavings still had a slight brown colour.

The relation between the coloration obtained in the "fuming" process and the tannin content of various kinds of oak.

It is well known that some varieties of oak "fume" much more easily than others, and great variations are found in this respect in different samples of wood said to be of the same origin. Borings from six samples of oak were subjected at the same time to the action of ammonia escaping from a solution of the gas in a large bell jar. The samples of wood employed were English (A), English (B), Japanese, American, Sap English (B) and Sap American oak respectively. The intensity of the colour obtained decreased in the order given. In the case of the Sap American oak no appreciable effect was produced.

The tannin content of the various samples was compared by extracting 2 g. of the finely ground borings with 100 cc. of water, the solution being heated for some hours in the water bath. The tannin was determined by the Löwenthal method, and in the case of the first experiments no allowance was made for "non-tans" present. The results obtained were as follows:

"Tannin" in 100 cc. of extract:

English (A)	English (B)	American	Japanese	Sap English	Sap American
0.08	0.076	0.04	0.025	0.024	0.005

On comparing these results with those obtained for the "fuming" effect it will be seen that they are in the same order, but the difference between the "tannin" content of the American and Japanese oak is greater than was expected from the appearance after "fuming."

In a later experiment, however, in which allowance was made for "non-tans" in the solution, by a combination of the Löwenthal and hide powder

detannisation methods, the tannin content of the extract of the American oak was found to be almost identical with that of an extract of the Japanese oak.

Absorption of tannin from oak extracts by silk and subsequent "fuming" of the silk.

In view of the affinity of silk for tannin it appeared of interest to investigate the action of silk on the extracts obtained from the various kinds of oak dealt with above. Pieces of white "Jap" silk 3 by 3 inches were heated in the extracts for several hours, removed and dried. One piece from each solution was then suspended in a bell jar containing a concentrated solution of ammonia and left overnight.

In the case of the "unfumed" silk light colours were obtained, but after "fuming," the colours varied from dark brown in the case of English oak (A) extract, through lighter brown to colourless silk in the case of Sap American oak.

The colours obtained after "fuming" in the case of the pieces of silk treated with extracts of Japanese and sap English oak were of approximately the same intensity, as would be expected from the tannin content of the extracts. In the case of the extract of American oak the "fumed" silk was rather lighter in colour than was expected.

It was found that, as was expected, tannin is not taken up as readily from these extracts by cotton as by silk, but is absorbed by lustre-cellulose (viscose), a fine light brown coloration being obtained on drying and subjecting to ammonia. These colorations obtained in silk appear to be fast to light and stable to dilute alkalis, they are bleached very slightly by dilute mineral acids. Washing in water does not give a coloured extract, and in this respect the "fumed" silk differs from "fumed" oak which gives a highly coloured extract on treatment with water.

It should be noted that this strongly coloured aqueous extract from "fumed" oak does not dye silk, only a very faint coloration being obtained on silk treated with this extract, even after "fuming" of the silk so treated. In this respect "fumed" oak differs markedly from natural brown oak, the extract from which dyes silk very readily.

On treatment of silk, which has absorbed tannin from an extract of English oak with ammonia in absence of air, the red coloration obtained in the wood is not produced, but the ordinary "fuming" effect is noticed. It is found, however, that, as would be expected, oxygen is absorbed by silk in the process of "fuming" by means of a solution of ammonia.

The action of methylamine and trimethylamine on oak.

In view of the fact that there is some resemblance between the colour of natural brown oak and English oak which has been treated with ammonia in absence of air, it seemed advisable to investigate the action of alkyl am-

monias on oak; more especially as the decomposition products of the nitrogenous constituents of the wood are likely to contain substances of this nature.

English oak treated with methylamine in absence of air showed a fine reddish brown coloration, and if this gas mixed with a limited supply of oxygen is allowed to act on the wood the colorations of various samples of brown oak are exactly reproduced. It is found, however, that oak treated in this way gradually darkens in colour on exposure to air, until finally the ordinary coloration characteristic of "fumed" oak is obtained. The results obtained by exposing various kinds of oak to the action of methylamine and a plentiful supply of air are similar to those obtained with ammonia, with the exception that in the case of English oak the coloration obtained at the commencement of the experiment is redder than when ammonia is employed. Trimethylamine gave results similar to those obtained with methylamine. Silk which has absorbed tannin from an oak extract may also be "fumed" by these substituted ammonias.

In order further to investigate the production of the reddish coloration in oak treated with ammonia or a substituted ammonia in absence of air, pieces of English (C) and (D), Japanese, American and Austrian oak were placed in a glass tube. The air was then exhausted from the tube and methylamine from a solution of the substance allowed to enter. After some time a reddish coloration appeared on both pieces of English oak, a very slight similar coloration on the American oak, and still less on the Austrian oak, but none on the Japanese oak. It thus appears that English oak more readily assumes the red brown coloration of natural brown oak than do the other varieties. On admission of air after several weeks the red coloration rapidly changed to the brown characteristic of "fumed" oak.

I am indebted to Mr Hamilton Smith of Messrs Heal and Son, Ltd., for the samples of oak used in this experiment, and for other samples of wood to be used later.

Natural brown oak.

Various samples of natural brown oak were employed in this investigation, for some of which I am indebted to Prof. P. Groom, others were obtained from freshly felled trees near Rickmansworth.

It has been mentioned that the coloration of natural brown oak, which is different from that of ordinary "fumed" oak, can be reproduced by the action of ammonia or a substituted ammonia on English oak, if oxygen is partly or wholly excluded during the interaction. It has also been pointed out that the colour so far produced in this way darkens when the oak is exposed to air, which is of course not the case with natural brown oak. It is possible, however, that in the natural brown oak the tannin is combined with a base of greater complexity than the substances so far employed, and this red compound in the wood may not become oxidised on exposure to air. Various experiments were carried out in order to find out whether or not the

coloration of natural brown oak is due to the interaction of the tannin of the oak with such nitrogenous compound.

In the first place, in view of the fact that an organism is concerned in the production of natural brown oak it seemed possible this oak might contain more nitrogen than "white" oak; but so far no conclusive evidence has been obtained that this is the case, as will be seen from the results given below:

Percentage of nitrogen in various kinds of dry oak:

Brown oak (A)	(B)	English oak (A)	(B)	(C)	Japanese oak
0.404	0.343	0.388	0.344	0.331	0.386

These results are in all cases the mean of two determinations which were in close agreement. Although in some cases the amount of nitrogen in the "white" oak is as great as in the brown, it should be noted that the brown oak (A) and the white oak (C) are from the same tree, and in this case there is a considerable difference in the amount of nitrogen contained in the wood.

Examination of extracts from brown and white oak.

(a) *Aqueous extracts.* If the excess of nitrogen in the brown oak (A) as compared with the "white" oak (C) were due to the accumulation of ammonium compounds, it would be expected that considerably more ammonia would be obtained from an aqueous extract of brown oak than would be obtained from "white" oak extract on distillation with an alkali.

The amounts of free and albuminoid ammonia in 25 cc. of a cold water extract of shavings of the two kinds of oak were very small, but the ratio of the free ammonia in the extract of the brown oak to that in the other extract was 2.4 : 1 and the albuminoid ammonia 2.3 : 1. In very dilute hydrochloric acid extracts of the wood the ratios were similarly 2.1 : 1 and 1.4 : 1. Owing to the very small amounts of ammonia obtained in this way it is, however, impossible to draw any conclusion as to any connection between the ammonia content of these extracts and the colour of natural brown oak.

In view of the possibility that the coloration is due to the action of a nitrogenous substance other than ammonia, it was thought that evidence of such interaction might be obtained by determining the total nitrogen in extracts of brown and white oak, more especially as the nitrogen added to oak in the form of ammonia in the ordinary "fuming" process is removed when the "fumed" oak is extracted with water.

In this experiment 5 g. of cross grain shavings were shaken intermittently with 100 cc. of distilled water for three days. The nitrogen in the filtered extract was then determined by the Kjeldahl process.

Extracts from two samples of natural brown oak, English and Japanese oak, were employed in this experiment. The amount of nitrogen in the residues obtained from the extracts was very small in all cases, and although more nitrogen was found in the residue from the brown oak extract the amount of this nitrogen was not sufficient to justify any definite conclusion as to the part played by the nitrogenous constituents of the wood in the production

of the brown colour. Distillations in steam of "white" and brown oak from the same tree were carried out, but no appreciable differences were noted in the distillates so obtained.

It is to be noted that cold water extracts of brown oak contain only about two-thirds of the amount of acid (phenolphthalein as indicator) contained in similar extracts of "white" oak from the same tree. In view of the fact that absorption of oxygen by tannin with the production of coloured substances takes place in alkaline solution, the greater acidity of the "white" oak extract may be of some importance. This point will be investigated further from the point of view of hydrogen ion concentration of the extracts.

(b) *Alcoholic extracts.* 5 g. of cross grain shavings of two samples of brown oak, white English oak, and Japanese oak were extracted with 100 cc. of absolute alcohol for three days with intermittent mechanical shaking. As is the case with the aqueous extracts the alcoholic extracts from the brown oak are deeper in colour than the extracts from the white oak. This point is referred to later in connection with the ultra-violet absorption spectra of the extracts.

The nitrogen content in the residues obtained from the alcoholic extracts was extremely small in all cases, and was found to be rather less in the extracts from the brown oaks than the white.

It thus appears from these experiments that although a colour similar to that of natural brown oak can be obtained by the action of ammonia or a substituted ammonia on English oak under certain conditions, the production of this colour in nature is probably not entirely dependent on the nitrogenous constituents of the wood.

The dyeing of silk by means of extracts from natural brown oak.

It has been pointed out that an aqueous extract of natural brown oak, unlike the strongly coloured extract of "fumed" oak, dyes silk readily, but the silk dyed with an extract of natural brown oak already shows the colour of "fumed" silk, and is not altered in depth to any appreciable extent on exposure to ammonia and air. Further investigation of this point is in progress.

Effect on English oak of prolonged heating in the hot water oven.

It was found that if pieces of English oak were heated intermittently in a hot water oven for several weeks the colour of the wood gradually darkened until it became identical with that of some varieties of natural brown oak. It is known that coloured substances, "oak reds" or phlobaphenes, which occur in oak bark, and to a limited extent in oak, are produced by elimination of water from tannins. References to the production and properties of these substances are given by Freudenberg [1920]. Some of these tannin "anhydrides" are slightly soluble in water and others are insoluble. Their chemical constitution appears to be unknown. In order to investigate the possibility

of the colour of natural brown oak being due to the presence of "oak red," silk was treated with extracts of natural brown oak, English oak heated several weeks in the steam oven, and oak bark. Silk dyed in these extracts had, before "fuming," similar colours in the case of the natural brown and heated oak, but in the case of the bark extract the colour was much redder. The silk from the bark extract had, after "fuming," a colour quite different from ordinary "fumed" silk, and almost identical with that of the wood of the natural brown oak used in the experiment.

This result considered in relation to the results referred to in connection with the nitrogenous constituents of the oak, and the results obtained in the spectroscopic examination referred to later, would appear to indicate that the colour is partly due to the presence of oak reds, or phlobaphenes, and partly to the interaction of the tannin with a nitrogenous base in the wood, but further investigation is necessary before any definite conclusion can be reached.

The ultra-violet absorption spectra of oak extracts.

It was hoped that some information as to the cause of the coloration in natural brown oak might be obtained by a spectroscopic investigation of various oak extracts. For the use of the ultra-violet spectrograph employed I am indebted to the Government Grant Committee of the Royal Society. Photographs of the ultra-violet absorption spectra of extracts of "white" and brown English oak, heated English oak, and of oak bark were taken. In the solutions so far examined definite absorption bands were absent, but considerable general absorption was shown, more especially with brown oak and bark extracts. For investigation of the ultra-violet absorption spectra 1 g. of finely ground material was extracted with 100 cc. of water for 24 hours with intermittent heating. The extracts were filtered and diluted with an equal volume of water. The ultra-violet absorption spectra of the extracts of brown oak and oak bark from a "brown" oak tree were almost identical, and the absorption of the extract of heated English oak was intermediate between that of the extract of English oak and that of brown oak extract.

In the absence of characteristic absorption bands it is difficult to draw definite conclusions from these results, but they would appear to indicate that the natural brown oak and bark from a brown oak tree give up the same colouring matter to water, and that by heating the English oak some of this colouring matter is produced.

SUMMARY.

The production of the brown coloration on "fumed" oak is due to the combined action of the ammonia employed and atmospheric oxygen. English oak treated with ammonia or a substituted ammonia in absence of oxygen shows a reddish coloration which is, however, changed on exposure to air with production of the ordinary coloration of "fumed" oak; other varieties

of oak either do not show this red coloration at all or only to a very limited extent.

The relation between the tannin content of various kinds of oak, and the coloration produced on "fuming," has also been investigated, together with the absorption of tannin from oak extracts by means of silk, and the subsequent "fuming" of the silk.

From the results obtained so far it appears that the reddish brown colour of natural brown oak may be due partly to the interaction of the tannin with a nitrogenous compound in the wood, and partly to the presence of a phlobaphene.

The investigation outlined above is being continued and extended to include the action of ammonia on other varieties of wood.

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