THE BLEACHING OF FLOUR.

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A CASE recently tried before Mr Justice Warrington (The Flour Oxidising Co., Ld. *v.* J. and R. Hutchinson) has brought to light, what I do not imagine is a matter of common knowledge, namely that large quantities of flour both in this country and abroad are artificially bleached in order it would appear primarily to satisfy the fancy of the public for white bread. The popular taste for the appearance of their food naturally leads the caterers to satisfy it; the yellowness of milk and its richness are usually associated together in the mind of the man in the street consequently it is very difficult now-a-days to purchase milk which has not been artificially coloured.

The similar public taste for whiteness in their bread was met until comparatively recently by keeping the flour after grinding for six to eight weeks; in this time what is technically termed "conditioning" of the flour occurs; the flour becomes whiter, and its baking qualities are simultaneously improved. In 1901, however, a patent was granted to John and Sydney Andrews of Belfast which is now the property of the plaintiffs in the recent action. It cannot be doubted that this patent is of very considerable pecuniary value for it enables the miller to accomplish in a few minutes the whitening that previously occupied a couple of months. The defendants in the action were also millers and it was alleged that they had infringed the plaintiffs' patent by using a similar process which in the case was spoken of as the Alsop process. Both processes have this in common that the flour is bleached by exposing it to the action of peroxide of nitrogen fumes.

The subject has been a matter of previous litigation, the Court of Appeal and the House of Lords having decided that the Andrews'

patent is valid, and a similar result followed the case to which I have alluded. After a hearing which occupied twenty-six days, Mr Justice Warrington pronounced judgment in favour of the plaintiffs.

Into the technical and legal questions involved, and upon which this judgment mainly rests, it is no part of my duty to enter. But any problem which deals with the food of the people raises questions affecting the public health, and it was this side-issue upon which I was asked to give evidence on behalf of the defendants' case, and which I propose to treat in the present article.

I have consistently for many years raised my voice whenever possible against adulterations, and against the use of antiseptics and preservatives in foods, on the ground that they are prejudicial to health especially in producing an increased difficulty of digestion due to the inhibiting action preservatives have on digestive enzymes. The stringent laws of the United States against the employment of adulterants of this order have met with my sympathetic approval, for if they err at all, it is an error on the right side, for they prevent the introduction of even the thin end of the wedge.

I must confess that to the non-legal mind it was a little difficult to see why the defendants in the recent action should have made it a part of their case to show that nitrogen peroxide had a deleterious action on the flour seeing that they were themselves anxious to use what was practically the same method for bleaching. So far as I have been able to unravel the legal subtleties of the case, it appears, however, that if they had been successful in proving this point, they would have established that the specification of the patent was so far incorrect, and therefore the patent itself would have been rendered invalid.

The important question for the hygienist is, however, far removed from the purely commercial aspect of the case, and resolves itself into the enquiry whether treatment with nitrogen peroxide does or does not injure the flour in such a way as to render it injurious to the consumer. If the answer to this question is in the affirmative the employment of this method of artificial ageing ought to be prohibited quite independently of the claims of rival patentees.

The process of natural ageing appears to produce two important changes, which are not disputed. One of these is that the flour becomes whiter, and the second is that its "baking qualities" are enhanced. Whether it produces any difference in the digestibility of the bread does not appear to have been specially investigated; one can, on this point therefore, only say that anything that increases the attractiveness

of a food, will other things being equal provide that psychical stimulus which we know is so important in matters of appetite and digestion.

The upholders of the process of artificial ageing maintain (1) that the flour is whiter than freshly ground flour, (2) that the baking qualities of the flour are equally good or better than those of flour naturally aged, and (3) that any effect on digestibility is negligible.

The first of these three propositions is undisputed.

The second is a matter for the bakers and furnished them with the opportunity of demonstrating that "expert" witnesses in this class of the community are not free from the suspicion that their opinions are influenced by the side which happens to have retained their services, a failing which is not confined to "expert" bakers and millers. Certainly the loaves exhibited did not convey much to the non-experts in court. The differences in the appearance of the loaves are of that unimportant kind the detection of which requires the practised eye.

The third question, the one relating to digestibility and possible chemical alterations produced by the reagent employed, was the one on which my opinion was sought, and I consented to give it as it afforded me another opportunity to enter my protest against the doctoring of an important food stuff.

When I was first asked to give evidence, I was entirely unaware of how extensively artificial bleaching of flour is employed; I fondly considered that at least the staff of life had escaped the attention of the decorative artist; moreover I knew nothing from personal experience of the effect of the bleaching process, and therefore I undertook a few experiments in order to test the matter in dispute. The time afforded me for the purpose was far too short, and I sincerely wished as the case proceeded, and especially when under the stress of cross-examination, that I had had six months to work at it, with nothing else to do, instead of about the same number of days which were already largely occupied with other work. The small number of observations I was able to make confirmed those published in America by chemists who have worked at the question more thoroughly; I cannot see my way at present to undertake any further investigations on the subject, but my observations such as they are appear to me to be worthy of record in a scientific journal. The conclusions I have drawn from my own observations and from those of others are briefly, (1) that the reagent employed comes under the heading of preservatives, and by the inventors this is regarded as an advantage; (2) that the presence of nitrogen peroxide or the products of its action on flour (nitrite reacting material) is distinctly unfavourable

to the activity of digestive enzymes and (3) that the action of the reagent is to produce a change in certain constituents of the flour which impairs their readiness of digestion and therefore their nutritive value.

Admitting all the above, it is only fair to grant on the other side that the total amount of such changes in the flour is small, and that the amount of nitrite left in the flour is only as a rule a few parts per million, and even that small amount is reduced by one half in the process of baking. The diminution in digestibility and nutritive value is therefore not very considerable for a healthy adult with normal digestive capacity. Whether the change is sufficient to be serious for infants or invalids is a question upon which there is at present no evidence, although that possibility should always be borne in mind; may be in such cases the old adage about the last straw may be applicable.

If the process of artificial bleaching sanctioned as it now is by law becomes universal, it should at least be confined within the narrow margin just mentioned. Cases have occurred where over-bleaching has considerably exceeded these limits, and the public do not appear to have any guarantee of the amount of bleaching practised in the preparation of any particular flour. What the miller at present cares most about is the whiteness of the product.

The following brief extract from Mr Justice Warrington's judgment puts the matter in a nutshell.

"Even Dr Halliburton did not go further as a summary of what he considered to be the result, than that the process of treatment by the plaintiffs' invention imposes on the human frame just one more of those extra burdens which the progress of civilisation has from time to time imposed on the human frame. Many of us think that there are many modern improvements, the introduction of motor cars, for example, which impose an extra strain on the human frame, but no one would pretend to say that a patent for the invention of a motor car would not have been a useful invention for that reason. With regard to digestibility it seems to me, it is not a practical objection, and even if it is made out that there is a scientific and theoretical action on the flour which may be said to be deleterious, there is no evidence that there is any practical substantial deleterious result of which I can take account."

That really is the crux of the whole question, and those interested in hygiene will have to see in the future that the scientific objection never becomes practical and substantial, just as some of our public authorities are attempting to minimise the dust, smell, noise and other discomforts that attend the use of motor omnibuses.

In certain of the American States, the use of artificial bleaching of flour has been prohibited in accordance with their law against the employment of even traces of preservative materials. However much we should like to see such an ideal made universal, it is necessary for us as practical men to remember that ideals are not always realisable in older countries, where even more necessary and urgent reforms of the law are difficult to attain.

Passing, however, from generalities, to what after all is the main purport of this paper, we will first consider briefly the results of a scientific kind obtained by others in connection with the subject, and finally the experimental work which I have performed myself.

The most extensive work on the effect of artificial bleaching by peroxide of nitrogen has been carried out by Dr Ladd, Professor of Chemistry, who occupies the position of Food Commissioner in the State of North Dakota, and confirmatory experiments so far as digestibility is concerned have been performed by Dr Shepard, Chemist of the South Dakota Experiment Station. These researches have been published in numerous Government Bulletins, but they are also summarised in recent issues of the *Chemical News*[1].

Professor Ladd's main conclusions are:

1. That the amount of nitrite reacting material left in the flour varies a good deal; in over-bleached specimens such as may be obtained from flour left in the separators and so frequently subjected to the action of the fumes, there may be even a xanthoproteic reaction produced.

2. The oil expressed from the flour contains nitrogen and its iodine absorbing value is increased.

3. The digestibility of the starch and gluten as tested by artificial digestion by means of diastase, ptyalin, pepsin and trypsin is diminished.

4. The proportion of amino-nitrogen to protein-nitrogen which diminishes during natural ageing remains unaltered or is increased.

This conclusion has been disputed by chemists both in America and this country, and no doubt it is a difficult point to determine accurately for the change is admittedly a small one. In the state of our present knowledge concerning the reversibility of enzyme action, it is possible that both changes may occur either during the ripening of the grain, or even after the grain has been ground into flour. The smallness of the change in either direction makes this particular factor one of negligible importance from the nutritive standpoint, but if Dr Ladd's statement is correct, it helps to establish the contention that artificial

[1] March 6, 13 and 19, 1909. See also Ladd and Bassett, *J. Biolog. Chem.* VI. 75, 1909.

ageing is a different process from the natural one, and much the same may be said regarding the change in the oil, which apart from the part it plays as a flavouring agent is quantitatively unimportant.

5. No actual chemical change could be detected in the starch.

6. The change in the gluten is partly physical, partly chemical. The gluten washed out from bleached flour is not smooth, but knotty, and its water absorbing power is lessened, so that from the baker's point of view it does not make so good a loaf; this, however, is disputed by rival bakers. It is suggested that the chemical change is of the nature of a diazo-reaction, for nitrogen is evolved on treatment with an acid.

7. The diminution of digestibility is due partly to the presence of nitrous acid or nitrite reacting material acting inhibitingly on digestive enzymes; and partly to the fact that the chemical change produced in the gluten renders it more difficult of solution in digestive juices.

8. The loss of digestibility in the bread made from bleached flour though present is less marked than in the flour itself.

Sufficient of these statements have been proved in American courts of law to render the future use of nitrogen peroxide as a bleaching agent prohibitive in the future in certain States.

Dr Ladd has, however, gone further than this and states that a highly concentrated alcoholic extract of flour which was purposely over-bleached in order to magnify the result was fatal to rabbits, their stomachs showing signs of corrosive poisoning. A fatal result followed a similar experiment with a specimen of commercially bleached flour. Others in America have repeated these experiments on animals but with negative results. Drs Luff and Willcox following minutely the directions of Dr Ladd with specimens of flour bleached in this country have also obtained negative results. One naturally attaches more importance to one positive than to many negative findings, but even admitting that Dr Ladd is correct, the amount of toxic material, seeing that his extracts were enormously concentrated, is so small, that one cannot find fault with Mr Justice Warrington when he regards such experiments as bearing on the theoretical rather than on the "practical and substantial" aspect of the question.

My own investigations have been entirely on the question of digestibility, the experiments being made *in vitro*, not *in vivo*, and I was much surprised at the very great lessening of enzymic action which occurs in the presence of quite minute amounts of nitrites.

The first experiments I performed related not to flour but to starch and protein to which small quantities of sodium nitrite were added.

I selected saliva as a type of a starch-digesting fluid, and gastric juice as a type of a protein-digesting fluid.

Equal quantities of dilute starch paste were placed in a series of tubes, and a small equal amount of saliva added to each. Some tubes had no further addition, but others had added to them small quantities of sodium nitrite in the proportions 1 : 1000, 1 : 2000 and so on down to 1 : 32,000. All were then placed in the incubator at 40° C., and tested from time to time to determine the achromic point, that is the instant when the mixture ceased to give any colouration with iodine. This point was reached in the control tube in 18 minutes; in the tube containing nitrite (1 : 32,000) it was not reached until 33 minutes. The time became still longer in the remainder increasing with the concentration of nitrite.

The protein selected for preliminary experiment was fibrin stained with carmine (Grützner's method); a number of parallel tubes were arranged as before differing only in the amount of nitrite added; the hydrochloric acid of the artificial gastric juice would produce from this some liberation of nitrous acid. The depth of the tint owing to the liberation of the carmine from the fibrin undergoing solution was taken as a measure of digestive activity. In tubes containing one part of nitrite (reckoned as nitrous acid) in 8000 digestion was entirely prevented; a small amount of digestion occurred over night in the tube containing 1 part in 16,000, and a small amount occurred in an hour in the tube containing 1 part in 32,000, but this by colorimetry was found to be only one seventh part of that which had occurred in the same time in the tube containing no nitrite.

Seeing that nitrous acid and its salts produce no known chemical action on starch, their inhibiting action on its digestion by amylolytic enzymes can only at present be explained by their action on the enzyme.

But in the case of protein there are two possibilities, action on the enzyme and action on the substrate (protein).

The question I next set before me was therefore this—Does previous treatment of a protein with a nitrite delay its subsequent digestion, even although there may be no actual nitrite present during the digestion experiment?

I therefore took equal quantities of fibrin stained with carmine as before and placed each in the same volume of 0·1 per cent. hydrochloric acid, a strength of acid which in itself causes no appreciable amount of digestion in many hours. To some of the specimens I added one part of sodium nitrite in 16,000, a strength I had previously found delayed digestion markedly. All of these were allowed to stand at 40° C. over

night; the hydrochloric acid would liberate some free nitrous acid from the nitrite, and so would roughly imitate the treatment which flour undergoes during artificial bleaching.

The next morning, some of the specimens to which nitrite had been added were washed entirely free from the liquid in which they had been standing, and then fresh 0·1 per cent. hydrochloric acid in the same quantity as before was added.

My tubes were now in three sets:

1. Those with nitrite.
2. Those previously treated with nitrite.
3. Those to which no nitrite had been added.

Pepsin was added in equal quantities to each and the whole placed in the incubator at body temperature for one hour. The depth of the red tint of the filtered fluid indicated as before the extent of digestion.

The results were as follows:

In set 1, the amount of digestion was very slight.

In set 2, the amount of digestion was slight, but greater than in set 1.

In set 3, the fibrin had almost entirely dissolved and the liquid was consequently deep red.

The results were so striking that I exhibited the tubes in court.

I further investigated the effect of sodium nitrite on the rennet enzyme, and found that the inhibiting effect on its action almost negligible.

The addition of sodium nitrite even up to 1 part to 4000 of milk did not delay the time of curdling; but if the same addition of nitrite (no means being taken to liberate free nitrous acid) is made to the milk 12 hours previously, the time of curdling was nearly doubled.

I think these experiments show that both factors have to be reckoned with, namely:

(1) The presence of nitrous acid (even in the comparatively innocuous form of a salt) hinders enzyme action.

(2) Previous treatment with nitrous acid alters a protein in such a way as to render it less readily susceptible to the solvent action of digestive juices.

Passing now to experiments on flour, I selected at random from the large number of specimens sent to me four samples of unbleached flour, and four of bleached flour, with which to carry out parallel experiments. I knew nothing at the time of the amount of nitrite in the bleached specimens.

I first determined the achromic point during salivary digestion carrying out the experiment in the same way as with starch. The achromic point occurred in the following times :

Sample 1.	22 minutes	Average for the unbleached specimens 23½ minutes.
,, 2.	25 ,,	
,, 3.	21 ,,	
,, 4.	26 ,,	
,, 5.	32 ,,	Average for the bleached specimens 35½ minutes.
,, 6.	36 ,,	
,, 7.	29 ,,	
,, 8.	45 (?) ,,	

The rate of digestion is thus distinctly delayed in the bleached samples.

In regard to the digestion of gluten I found considerable difficulty; for gluten separated from flour is adhesive, intractable and difficult of access to any solvent that tries to penetrate it. The carmine method, which I at first attempted, failed because the dye will not penetrate gluten.

Dr Ladd has employed the following method which strikes me as an ingenious one for overcoming the difficulty; the bottom of a piece of wide glass tubing is plugged with glass wool, and on the plug is placed the pellet of gluten to be digested. This is immersed in a flask containing the digestive solution, and the time is noted when the gluten disappears.

Not knowing of this method I had recourse to the following:—

The same eight flours were taken as before, gluten was prepared from each and the moisture in a part of each specimen of gluten determined in the usual way.

An amount of moist gluten corresponding in each case to 5 grammes of dry gluten was then submitted to artificial gastric digestion, the conditions being parallel throughout. Sixteen hours later, the undigested residue was caught on a filter which had previously been dried and weighed. The filter *plus* the undigested residue was dried to constant weight, and again weighed; the weight of the filter was deducted, and the undigested residue was found to be as follows in the eight specimens. The experiment was done in duplicate, and the figures given are the mean numbers.

The comparative indigestibility of the gluten from bleached specimens comes out quite clearly. It will be further noted that the loss of digestibility is not proportional to the amount of nitrite reacting

material present in the flour, the figures for which are given in the last column. These figures I was subsequently supplied with and represent the mean results obtained by two analysts (Dr Hehner and Mr Gordon Salomon). From this one would judge that the main deleterious action is exerted by the nitrous fumes while in contact with the flour, and the diminution of digestibility does not depend on the more or less accidental quantity left behind.

	Undigested residue	Average	Parts of nitrite reckoned as sodium nitrite per million of flour
No. 1.	3·01 grammes		0
„ 2.	3·35 „	Unbleached	0
„ 3.	3·2 „	3·245 grammes	0
„ 4.	3·42 „		0·1
„ 5.	3·52 „		5
„ 6.	3·67 „	Bleached	2·5
„ 7.	3·82 „	3·662 grammes	1·9
„ 8.	3·64 „		1·3

It will further be noted in the preceding table that one of the unbleached flours contained a trace of nitrite; this apparently was a case of accidental contamination, for the flour came from a factory where the bleaching process was in use. It will be seen that this flour gives the worst result of the four unbleached specimens.

The only other experiment I have performed was a comparison of two flours from the same grist, one of which was freshly milled, and the other was milled three months previously and therefore had undergone natural ageing. In the determination of the achromic point, the differences obtained are within the limits of experimental error, the times being in two samples of the freshly milled flour 18·5 and 17 minutes, and in two samples of the aged flour 18 and 17·5 minutes respectively.

A gluten digestion experiment carried out in the same way as that already described gave the following mean results. The undigested residue from 5 grammes of the gluten from the freshly milled flour amounted to 3·491 grammes; and that from the gluten of the naturally aged flour was 3·482 grammes. The difference here also will be seen to be negligible.

Having no appliances in my laboratory for baking I carried out no experiments on the comparative digestibility of the bread made from different flours. The results obtained by those who have had the opportunity of examining the breads show that the lessening of digestibility of the bread is less marked than it is in the flour. This

appears to be partly due to the reduction of the amount of the nitrite reacting material which occurs during baking, and in reference to the protein (gluten) one can only suggest that the process of baking increases the difficulty of digestion of that substance even in unbleached specimens, so that any difference in digestibility between a loaf made from it and one made from bleached flour would not be so noticeable. It can hardly be doubted that this, which after all is the most important question from the standpoint of the consumer, has had considerable influence with judges in deciding as they have that the objection to artificial bleaching is more or less theoretical. But knowing as we do the possible practical dangers which might ensue were millers allowed a free hand in the use of the very strong reagent they employ, it is necessary that a strict watch should be exercised to keep its use within the limits of safety.