

One and a half grams of the alcohols obtained from Chinese wax, 0.3 gram of fatty acid and 2 cc. of the reagent solution were heated as in the foregoing experiments and required 1.00 cc. of standard alkali to neutralize, showing that the fatty acid had been completely esterified to within the limits of accuracy of the test. I took pains to prove that the free acidity was really due to the SO_3H , radical.

Amyl alcohol is slowly evaporated from an open flask on a water-bath, but if a sufficient excess is used, fatty acids can be completely combined with this alcohol.

About 1.2 grams of fatty acid and exactly 2 cc. of the naphthalene-stearosulphonic acid solution were heated in an open flask on the water-bath. As soon as the bottom of the flask appeared dry about 2 cc. of amyl alcohol were added and the heating continued 4 hours. On adding neutralized alcohol and titrating it was found that 1.04 cc. of standard alkali were required, which corresponds closely to the acidity to methyl orange of 2 cc. of the reagent.

As might be expected the acids of rosin are not esterified by this method.
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A CONTRIBUTION TO THE CHEMISTRY OF THE BLEACHING OF FLOUR.

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Introduction.

For some time the writer has given more or less attention to the bleaching of flour. On withdrawing from the work of the Nebraska Experiment Station it seems desirable to publish the results at hand. The work is being continued by my colleague in the University and successor as Chemist of the Station, Dr. F. J. Alway. I am under obligations to him for valuable suggestions and for a part of the data here presented.

For many years proposals have been made and patents issued for bleaching cereal products with sulphur dioxide. British patent to Beans No. 2,502, issued in 1879, appears to be the first to mention chlorine as a bleaching agent. Modern bleaching of flour may be regarded as dating from 1898. French patent No. 277,751, issued to Frichot, discloses the use of nascent oxygen in a gaseous condition to be brought in contact with the flour in a finely divided state. Ozone is the chemical substance especially mentioned. It is recommended that ozone be prepared by electricity. British patent No. 1,661 to Andrews, discloses also the use of nascent oxygen and recommends the use of nitrogen peroxide as a bleaching agent. U. S. patent to Alsop No. 759,651, of 1904, discloses the use of air treated by electricity. The general introduction of bleaching into American mills dates from about the time of the last-named patent.

All commercial bleachers, in so far as I can ascertain, now use nitrogen peroxide, produced either chemically or by the action of electricity, and mixed with a large excess of air, as the bleaching agent.

Experimental Part.

Comparison of Bleached with Unbleached Flour.—Of a number of samples examined the following two may be taken as representative. Both samples were milled from the same lot of wheat and were as nearly identical as could be obtained, except that one sample was submitted in the usual commercial way to an electrical bleaching process. It was perhaps bleached less strongly than the average commercial sample. The other sample was not so treated.

	Treated.	Untreated.
Moisture.....	10.88	10.76
Ash.....	0.42	0.42
Ether Extract.....	1.03	1.04
Nitrogen.....	1.82	1.82
Crude Fiber.....	0.32	0.31

The result of the analyses shows that the samples were practically identical within the limits of error of the methods employed, which were those of the Association of Official Agricultural Chemists.

The treated flour was distinctly lighter in color than the untreated flour. A baking test gave loaves of practically identical size, weight and texture.

The untreated flour contained no nitrites. The treated flour was found to contain in one million parts of flour 0.78 of one part of nitrite, calculated as sodium nitrite.

The Relative Efficiency of Various Agents.—Samples of the unbleached flour were treated with the following substances, which have been proposed as bleaching agents.

A current of very carefully purified oxygen was passed through the flour heated to a temperature of 98°. No bleaching effect could be observed in the course of an hour, or as long as treated. The bleaching effect ascribed to oxygen is to be attributed to traces of chlorine which are usually present, if the gas is not most carefully purified.

Ozone—as Fleurent¹ has also pointed out—does not bleach flour. Ozone prepared by electricity from air, or oxygen containing a trace of nitrogen, contains nitrogen peroxide². The bleaching effect ascribed to ozone is to be attributed to the nitrogen peroxide present.

Pure carbon dioxide is without effect on the color of flour.

Bromine bleaches effectively. 4 cc. of bromine vapor at 25° mixed with three liters of air will distinctly bleach a kilo of the flour under consideration. 150 cc. have the maximum effect. When more than 900 cc. were applied the flour began to darken.

Chlorine deported itself similarly in all respects to bromine.

¹ Fleurent, *Northwestern Miller*, December 6, 1905.

² Shenstone and Evans, *J. Chem. Soc.* 73, 246 (1898).

Sulphur dioxide bleaches very slowly and requires a large excess. An efficient bleaching can be obtained, as this agent used in excess does not have a tendency to discolor the flour. Its odor is very pronounced in flour bleached by its use.

Nitrogen peroxide is most conveniently measured as nitric oxide. 3 cc. of nitric oxide gas mixed with three liters of air will efficiently bleach a kilo of flour. The maximum bleaching effect was obtained by the use of 40 cc. After this the color of the flour was gradually injured as the quantity of the nitric oxide was increased.

The maximum bleaching effect, without regard to the quantity of the reagent, can be obtained by the use of bromine. The other reagents follow in the order named: chlorine, sulphur dioxide, nitrogen peroxide. A given weight of nitrogen peroxide will bleach a far greater quantity of flour than the same weight of any of the other reagents mentioned. All samples of flour bleached with nitrogen peroxide, in-so-far as tested, respond to the Griess test for nitrites. Samples stored in laboratories, and in mills where bleachers are used, commonly respond to the same test. A sample exposed, however, for 13 months in an office not containing any electric or gas lights failed to respond to the Griess test.

A sample of the flour under consideration was placed in a layer $1/64$ inch thick between plates of glass. The plates were bound together at the edges with adhesive tape. The whole was exposed to the action of sunlight by placing in direct sunlight and reflecting also the rays against the reverse side by a mirror. The sample was bleached by an exposure of two hours.

Nitrogen peroxide mixed with an excess of ozone shows the same bleaching effect as when mixed with air. The bleaching is due solely to the peroxide present.

The Action of Certain Reagents on a Solution of the Coloring Matter from Wheat Flour.—The yellow coloring matter in wheat flour is dissolved in the oil of the flour. When the oil is extracted with benzene, ether, acetone or other solvents, the remaining part of the flour is nearly pure white. The solution of the oil has a bright yellow color. In the following tests a cold benzene extract was used.

A tube filled with the solution, containing no air except what may have been dissolved in the benzene, was bleached by exposing to direct sunlight for three hours.

A sample of the original bright yellow solution was bleached instantly by shaking with a very dilute solution of nitrous acid.

A sample was bleached more slowly than the preceding by shaking with dilute bromine water.

A sample was bleached slowly by exposing to the action of a solution of sulphurous acid in large excess.

Hydrogen peroxide solution, on shaking with the benzene solution of the oil and coloring matter, gave no bleaching effect. This was true in acid, neutral and basic solutions.

A solution of the colored oil in acetone was treated with a trace of water and aluminum amalgam. The color was not changed. Zinc dust and acetic acid were also without effect.

Action of Reagents on the Colored Oil.—The yellow colored oil, free from the solvent, may be rendered nearly colorless by very cautiously applying nitrogen peroxide, chlorine or bromine. The first effect is to destroy the yellow color. Secondary effects, such as causing the oil to become red-brown, are obtained by an excess of the reagent or by heating or by both.

Effect of Nitrogen Peroxide on the Constituents of Flour Other than the Coloring Matter.—Fleurent¹ found, in the study of what appears to the writer to have been over-bleached flours, that the iodine number of the oils was markedly decreased. Alway, in a private communication, states that he finds no apparent effect on the bread making qualities of numerous samples as actually commercially bleached in Nebraska.

The oil from bleached flour does not respond to the Griess test. The flour, after extracting with benzene, responds to the Griess test. The bread, after baking, contains nitrites, as found in this laboratory and as pointed out by Ladd². Evidently a part of the nitrous acid has formed a relatively stable compound. Presumably a salt has been formed by the union of nitrous acid with the mineral matter of the flour.

An excess of nitrogen peroxide discolors the gluten of the flour.

Conclusion.

The minute traces of yellow color present in flour can be bleached with different to ordinary oxidation or reduction or to acids or alkalis.

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Whatever the nature of the coloring matter may be it appears to be in such minute amounts of nitrogen peroxide that it is difficult to detect any effect on the flour other than the bleaching and the presence of traces of nitrites.

The extreme sensitiveness of the coloring matter to nitrous acid suggests that the color may be dependent on the presence of an amino group.

THE CHEMICAL COMPOSITION OF COOKED VEGETABLE FOODS.

PART II.

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The investigations described in the following pages, are a continuation of the work published in the *Journal of the American Chemical Society*,

¹Northwestern Miller, December 13, 1905.

²Bulletin No. 72, North Dakota Exp. Station.