THE VALUE OF THE HIGHER PHENOLS IN WOOD-PRESERVING OILS.

By SAMUEL CABOT.

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Recent investigators claim that the tar acids in creosote oils have little or no value for the preservation of timber. The reasons given are that the ingredients are volatile and somewhat soluble. This supposition is partially confirmed by analysis of preservative oils extracted from timber which have been in the ground for a long time. The extracts appeared to consist of heavy oils boiling above 250° C. and containing but a trace of phenols. The unsatisfactory part of these tests has been that in only a very few cases was the phenol content of the original oil known. In cases where the percentage of phenols was known, they were the lower carbolic and cresylic acids which are soluble and volatile. It does not appear that any investigator has claimed that the phenols are not the best wood preservative ingredients of creosote oil so long as they are contained in the wood. The only claim is that they have but temporary value. While this appears to be true of the lower phenols, the higher-boiling tar acids have a different character. Their fungicidal qualities are greater than the lower ones, their boiling points are very high and they are practically insoluble. The following experiments show that the phenols in high-boiling oils evaporate more slowly than the oil fraction in which they are contained.

Two grams each of heavy creosote oil and of phenols extracted from the same were exposed on a watch glass at a temperature of from 50–55° C. for two hundred hours and the loss of weight noted at stated intervals. The residue of oil left on the watch glass was a viscous fluid. That of the tar acids had a pitch-like consistency at 15° C. The following tables are taken from many giving similar results.

NO. 2 TAR ACIDS.

Temp.	Time. Hours.	Loss. Per cent.
50-55	1	1.35
50-55	4	3.5
50-55	7	7.6
50-55	12	8.8
50-55	15	10.2
50-55	18	10.5
50-55	43	15.6
50-55	67	18.8
50-55	94	20.8
50-55	140	23.0
50-55	164	24.3
50-55	188	25.3
50-55	200	25.75

NO. 1 HEAVY CREOSOTE OIL.

50-55	1	2.1
50-55	4	6.35
50-55	7	9.5
50-55	12	10.0
50-55	15	11.25
50-55	18	12.1
50-55	43	16.5
50-55	67	22.2
50-55	94	25.5
50-55	140	32.1
50-55	164	34.3
50-55	188	36.6
50-55	200	36.3

The tar acid residue in these experiments when boiled with a 35 per cent. solution of caustic soda was apparently insoluble. It was also insoluble in a 25 per cent. solution. Another portion of the tar acid residue was then dissolved in 90 per cent. of its weight of benzole, extracted with a warm 10 per cent. solution of caustic soda three times. The benzole became a dark translucent color, the caustic soda a clear brown and a black tarry layer remained between, after settling over night. The caustic soda extract was washed free from tarry matter with benzole, neutralized with sulphuric acid and extracted with ether in the usual way. This extract was found to contain less than 10 per cent. of the original tar acids dissolved in the benzole. It was found that the tarry layer was partially soluble in water, while the remainder after washing with water redissolved in benzole, showing that it had been dragged down only mechanically.

From these experiments it appears that the methods now in use for the analysis of creosote oil do not show the actual amount of higher phenols present, especially in oils extracted from wood for ascertaining the most permanent wood preservatives. A common practice is to redistill the oil and then analyze the distillate, disregarding the pitchy residue. The distillation would decompose the higher phenols to a considerable extent and as a greater part of them are non-volatile, they will supposedly be found in the pitchy residue. Again in the second step of the analyses a greater proportion of the tar acids could be dissolved in the caustic soda if a dilute solution were used and very much less in a more concentrated one. Under the most favorable conditions, however, it would be only a small part of the total.

The above experiments go to show that previous investigations referred to have found nothing to prove that the high-boiling phenols are not the most valuable ingredients in wood preservative creosote. On the contrary their gummy consistency gives them great physical advantage over straight oil, they are less volatile than the oil, are practically insoluble, and have fungicidal qualities far greater than any other of the products of creosote.

COMPOSITION OF DRY GLUTEN AND ITS RELATION TO THE PROTEIN CONTENT OF FLOUR.

By GEO. A. OLSON.

Received October 30, 1911.

In comparing the dry gluten and protein content of flour, Thatcher¹ found that the gluten content was in close agreement with the protein content of medium and high-protein flours ($N \times 6.25$), and frequently several per cent. lower in low-protein flours. Occasionally flours were found low in protein with a relatively high gluten content and *vice versa*. It occurred to the writer that perhaps the reason for high-protein flours containing relatively higher

¹ Wash. Exp. Sta., Bull. 84, 33.

glutens than did flours low in protein was due to a larger amount of impurities in the former.

It is needless at this time to enter into a complete historical account of the work done by different investigators along the line of gluten research. It might be well, however, to mention the fact that gluten as it is ordinarily prepared, according to Osborne,¹ contains besides "the greater part of the protein matter of seed, starch, fat, lecithin and phyto-cholesterin, and possibly some carbohydrate substance or substances of as yet unknown character. The chief constituents of the gluten are the two proteids, gliadin and glutenin. Norton² states that gliadin and glutenin make up about 75 per cent. of the true gluten of flour, the other constituents being non-gluten, mineral matter, fat, starch, fiber and other non-protein matter. Ritthausen³ found four proteids in gluten. Fleurent⁴ found three proteids, and Osborne and Voorhees⁵ found two proteids. Recent work by J. König and P. Rintelen⁶ support Ritthausen's views.

In our wheat and flour investigations at this Station it has been found that straight flour from Palouse wheats show variable gluten content, when compared with the protein content ($N \times 6.25$) of the respective flours. With these glutens at command and after a few preliminary experiments had been conducted, it was decided to investigate the reasons for the variations with a view of throwing some light on the baking qualities of the various flours under study. The glutens used for this series of investigations had been prepared by mixing 20 grams of flour and 12 cc. of water, allowing the mixture to stand for one hour, and then washing out the starch with a stream of water. A bolting-cloth was held beneath the kneaded dough in order to prevent the loss of the fine particles of gluten generally carried down with the water. After having removed as much of the starch as can possibly be done mechanically, the resulting wad of gluten was run over the bolting-cloth to pick up the fine particles. It is this gluten, after drying for twenty hours, which shows a variable quantity when compared with the protein of the flour.

The glutens studied were from flours representing wheats of the type of Bluestem, Red Russian, Turkey Red, Fife, Dale, Little Club, Galgalos and some of the Station hybrids. Particular attention was given to selecting flours containing average, high, and low glutens. No marked differences were observed in the comparisons between high-protein flours and their glutens, while on the other hand several flours with at least 10 per cent. protein ($N \times 6.25$) yielded glutens amounting to a little over 7 per cent. dry gluten.

Determinations of moisture, ash, starch and nitrogen were made of the different glutens selected. The

nitrogen and ash determinations were made according to the A. O. A. C. methods. Thoroughly dried samples of gluten were ground at a temperature of about 35° C. and finally capped tight in vials of the same temperature. The procedure eliminated moisture absorption to a minimum, while, on the other hand, it may have reduced the actual amount of moisture contained within the gluten. As comparative results were all that were desired, the writer can see no objection to the method, and the water thus found must have been either sealed up when drying the gluten the first time or water of combination.

The starch determinations were made by hydrolyzing the starch according to the writer's method¹ and the results thus obtained were in some cases checked by the Sachsse method.² Unlike starchy substances, such as feeding-stuffs, cereals, etc., it is difficult to determine the exact point of complete hydrolysis of gluten, due to the fact that comparatively little of the product enters into solution, thus making it difficult to observe the exact end point. With some judgment, however, little, if any, difficulty was encountered in the method. Repeated hydrolysis at different times gave results fairly concordant with those previously found. When compared with the Sachsse method no appreciable differences were observed. The peculiar reduction of the copper with the hydrolyzed gluten solutions will be discussed in the following paragraph.

Only a few of the copper reductions behaved like ordinary reducing substances when brought in contact with the Fehling solution, while, on the other hand, most of them produced flocculent precipitates on boiling, which were in some cases difficult to filter. The color of the reduced copper varied from a copper-red, light yellow to a dark brown. Those having the familiar copper color, and in every respect similar to sugar reduction of copper, are undoubtedly the hydrolyzed starch. Those having produced flocculent precipitates are no doubt admixed with some protein complex, probably mucoid-like substances or other protein loosely bound. The differences observed in different hydrolyzed glutens were quite marked, and repetitions gave similar characteristics in the same gluten as previously observed.

Repeated digestions of gluten with either calcium or barium hydroxide, filtering and precipitating the resulting filtrate with acetic acid, separating the acetic acid precipitate from liquid, followed by the hydrolysis of both precipitate and liquid with sulfuric acid and then neutralizing with sodium hydroxide, showed no reduction when brought in contact with Fehling's solution. According to this procedure neither a mucin nor mucoid-like substance could be confirmed.

The results of the analyses of the crude glutens representing flours made from different types of wheat have been summarized in Table I.

The data given in Table I clearly show that crude gluten has a variable nitrogen, ash, starch and

¹ Carnegie Inst., Washington, Pub. 84.

² *J. Am. Chem. Soc.*, 28, 8-25 (1906).

³ *J. prakt. Chem.*, 85, 213 (1862).

⁴ *Compt. rend.*, 1896, p. 327.

⁵ *Am. Chem. J.*, 15, 392 (1893).

⁶ *Z. Untersuch. Nahr.-Genuss.*, 8, 401-407 (1904).

¹ *THIS JOURNAL*, 1, No. 7 (1909).

² *Chem. Centr.*, 1877, 732; *J. Anal. Chem.*, 2, 153.

moisture content. The high starch content due to flocculent precipitation of copper should be attributed to other substance or substances than starch, the nature of which are as yet unknown.

TABLE I.—ANALYSES OF CRUDE GLUTEN MADE FROM STRAIGHT FLOURS.

	Per cent. N.	Per cent. ash.	Per cent. calculated as starch.	Per cent. water.
Average 24 samples.....	12.77	1.84	5.20	2.13
Maximum.....	14.09	3.08	12.70	3.82
Minimum.....	11.28	1.34	0.11	0.90

Although the results given in the above table do not show the variations in the amount of dry gluten compared to the protein content of the flour, comparable and extreme variations of gluten to protein of flour were nevertheless taken for this study. It might be of some value, however, before going further to state that abnormally low per cents. of dry gluten compared to protein of flour are not necessarily any richer in nitrogen, more free from ash, etc., than one equal to or higher in per cent. of gluten to protein of flour. The data for the nitrogen and protein of wheat and flour, the nitrogen in the gluten expressed in per cent. of the flour, and the per cent. of wet and dry gluten are summarized in the following table:

TABLE II.—DISTRIBUTION OF NITROGEN IN WHEAT, FLOUR AND GLUTEN AND PER CENT. OF GLUTEN IN FLOUR.

	Per cent. nitrogen in			Per cent. protein in		Per cent. gluten.	
	flour.			flour.		gluten.	
	Wheat.	Flour.	Gluten, in per cent. of flour.	Wheat.	Flour.	Wet.	Dry.
Av. 24 samples.....	1.89	1.73	1.29	11.81	10.81	30.82	9.88
Maximum.....	2.52	2.27	1.87	15.75	14.19	46.83	14.75
Minimum.....	1.33	1.29	0.86	8.31	8.06	19.39	7.20

It will be seen from the data given in the above table that percentagely the amount of nitrogen entering into the gluten make up is considerably less (74.6 per cent. of total nitrogen on an average) than that found in straight flours. The data further tend to show that flours high in protein are also high in gluten and flours of average protein composition or less yield percentagely lesser amounts of dry gluten than do flours of higher protein composition. Whether or not the gluten nitrogen is wholly made up of gliadin and glutenin nitrogen will be discussed at some other time.

It has been known for some time that in the process of washing out the starch from flour to get gluten, that some glutes have the tendency to scatter more than others, and as a result are difficult to gather into wads. Other flours, however, yield glutes with strong adhesive qualities and as a result tend to hold the gluten particles together in the process of washing. These characteristics have been attributed to the proportion of gliadin to glutenin contained in the flour.

Gluten determinations in flours of unusually low gluten content were repeated and it was found that these flours had a tendency to scatter and losses would vary, depending upon the care exercised in

washing out the starch from the flour. Undoubtedly some of the particles of gluten pass through the bolting-cloth as was indicated by an examination of the washings and the variable yields obtained in dry gluten. By indirect means it was possible to overcome the tendencies of the glutes to scatter. This was accomplished by mixing equal quantities of flour containing scattering gluten with one devoid of these characteristics. The weight of the wet and dry gluten in the non-spreading gluten flour being known, the weight of the wet and dry gluten in the other flour can be calculated from the results obtained with the mixture. The results obtained are as follows:

TABLE III.—COMPARISONS OF THE AMOUNT OF GLUTEN OBTAINED BY THE DIRECT AND INDIRECT METHODS.

No.	Direct.		Indirect.		Per cent. protein in flour.
	Per cent. wet gluten.	Per cent. dry gluten.	Per cent. wet gluten.	Per cent. dry gluten.	
3.....	20.78	7.66	26.95	7.66	8.19
5.....	12.78	4.63	23.17	8.94	8.19
11.....	22.54	8.88	23.11	8.54	8.19
23.....	21.51	7.23	21.12	9.49	8.06
24.....	20.00	6.94	24.64	8.81	8.13
25.....	12.70	4.44	27.35	9.40	8.19
27.....	20.69	7.16	20.85	7.76	8.06
28.....	19.29	6.70	18.79	7.30	8.19
34.....	25.51	8.82	28.98	9.59	9.88
37.....	13.30	4.57	18.81	6.40	6.38
38.....	18.04	6.41	31.28	10.00	8.56
39.....	12.44	4.40	21.20	7.36	6.56
43.....	17.89	6.25	21.09	6.85	8.06
47.....	26.54	9.61	39.78	13.86	12.13
62.....	24.37	9.40	35.04	11.58	10.31
64.....	27.69	9.59	33.22	11.68	11.38
68.....	24.94	9.52	39.36	12.86	10.44
69.....	30.53	10.97	39.84	12.63	11.88
70.....	18.93	7.09	26.58	9.60	8.75
72.....	19.99	7.30	32.20	10.78	8.06
76.....	21.40	7.95	33.28	11.19	9.88
78.....	20.72	8.01	35.08	11.38	9.94

In every case where the indirect method was put into use, results comparable with the protein content of the flour were obtained. The reason why the glutes of low-protein flours are several per cent. lower than in flours containing a medium or high-protein content is undoubtedly due to the scattering of the gluten and as a result a part of the gluten is lost, hence lower yields of gluten are recorded than are actually present.

The above method of blending flours, having glutes that tend to scatter, with flours having glutes with strong adhesive characteristics will give much higher yields of gluten, sometimes as much as 100 per cent. more than can be obtained by the direct process.

Those who make it a practice to determine the gluten content of flours and base their opinions on the results for the yield of gluten as obtained by the direct process are apt to obtain erroneous data, since at least 25 per cent. of the flours examined by the writer had glutes which tend to scatter in the process of preparation. It is, therefore, necessary to consider whether or not the glutes scatter and in such cases a blend with a strong flour will overcome the scattering tendencies, as well as give more correct

results than can be obtained by the direct method as it is commonly practiced.

CONCLUSIONS.

1. Gluten as it is ordinarily prepared has a variable nitrogen, ash, starch and moisture content.
2. The peculiar copper reduction resulting from adding the filtered extract from hydrolyzed gluten by acid is undoubtedly due to some other substance than starch or sugar.
3. An average of about 75 per cent. of the total nitrogen of flour enters into the crude gluten.
4. Glutens obtained from low-protein flours are not necessarily any richer in nitrogen, more free from ash, etc., than glutens derived from medium- or high-protein flours.
5. The reason why low-protein flours yield much lower per cents. of gluten than medium- or high-protein flours may be attributed to the scattering of such glutens, resulting in mechanical loss. By blending such flours with strong gluten flours, results in yields comparable to those obtained for medium- and high-protein flours.

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A COMPARATIVE STUDY OF METHODS FOR THE DETERMINATION OF HARD AND TOTAL SOFT RESINS IN THE HOP.

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Previous to taking up some chemical investigations at this laboratory it became necessary to devote some time to a study of methods for the determination of hard and total soft resins in the hop. Some very interesting results have been obtained which the authors think may be of value, especially to those connected with the brewing industry where the correct valuation of hops is of considerable moment. The results given may also be of some use to the work recently undertaken by a Committee of the International Barley and Hop Prize Exhibit at Chicago for the establishment of definite hop standards.

Previous investigations have shown that there are at least three so-called resins which are constituents of the hop cone, one "hard," tasteless resin and two "soft" bitter resins. Although a considerable amount of research has been done on the nature of these substances and their function in brewing, much is still obscure and in doubt. It is generally agreed, however, that the hard resin is of little or no commercial value, while investigations indicate that the major part of the real brewing value of hops lies in the soft resins, thus making their estimation of considerable importance.

In this study two different methods for the determination of both hard and total soft resins have been given a test: Briant and Meacham's¹ method and Siller's² method. The original volumetric method

of Lintner³ and the modified Lintner² method for total soft resins have also been studied. Although the original Lintner method has been shown to be inaccurate we have included it in this study because we have found from our correspondence that this method is still employed in a few instances. A method devised by us is given and the comparative results are reported. We have had good success in the use of this method, and while not claiming originality for the basic principles involved, we believe it overcomes some of the objections to present methods. For convenience it is here designated as "authors' method." Not all of the methods for the estimation of hop resins are given, but we believe all have been included that are receiving any extensive use.

METHODS.

In all the methods which have been devised for the determination of hop resins, the separation of the soft resins from the hard resin is dependent upon the ready solubility of the former in petrolic ether, the latter being practically insoluble in this solvent. The extraction of total resins from the hop is effected with ordinary ether.

Briefly stated, the methods compared are as follows:

Briant and Meacham's³ Method.—About four grams of hops are placed in a Soxhlet extractor and extracted for twenty-four hours with petrolic ether (boiling point 50° C.). After the extraction is completed the extraction flask is disconnected from the apparatus and its contents filtered while hot through a small filter paper into a tared wide-mouthed flask; the filtrate is then gently evaporated. The final drying operation is completed by placing the flask on its side in a hot water oven, where it is maintained at a temperature slightly above the boiling point of the ether until its weight is constant. The extract thus obtained is the total soft resins in the sample.

The hops left in the extractor from the petrolic ether extraction are next extracted with ordinary ether for 12 hours. The ethereal extract is then filtered into a tared flask, dried and weighed as in the previous extraction, the residue obtained being estimated as hard resin.

Siller's² Method. Soft Resins.—A ten-gram sample of hops which have been ground through a small meat grinder is placed in a Soxhlet extractor and extracted with petrolic ether (boiling point 30–40° C.) for 8–10 hours. The petrolic ether extract is then evaporated *in vacuo* on a water bath at 40° C. until all of the solvent is removed. The residue is then taken up with methyl alcohol to separate the wax present, filtered and made to 100 cc. volume. A 10 cc. aliquot (equivalent to 1 gram of hops) is placed in a weighed flask and the alcohol is then completely evaporated in a drying oven at 80°

¹ J. Fed. Inst. Brewing, 3, 233 (1897).

² Ztg. Untersuch. Nahrung-Gemiss., 18, 241.

³ Ztg. Ges. Brauwesen, 21, 407.

² Chem. Ztg., 32, 1068; O. Neuman, Wochenschrift für Brauerei, 1910.

³ Loc. cit.