PREPARATION AND PROPERTIES OF SULFATED WHEAT FLOUR[1]

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ABSTRACT

Ungelatinized sulfates of hard red winter wheat flour with sulfur contents ranging from 1.97 to 4.60% calculated as weight percent $-SO_3H$ were prepared in 80 to 90% yields by treatment with trimethylamine-sulfur trioxide in an aqueous system catalyzed by sodium hydroxide. The influence of temperature, time, catalyst concentration, and the amount of trimethylamine-sulfur trioxide on the extent of sulfation, yields, and properties of the flour sulfates are discussed.

The most distinctive characteristics of the sulfated flours are their high degree of dispersibility, high viscosity, and exceptional clarity in aqueous systems. Brookfield viscosities of 2% (by weight) aqueous dispersions of wheat flour sulfates at 25°C. and 30 r.p.m. ranged from 900 to 4,300 centipoises as compared to only 30 for unmodified wheat flour. Clarity of 1% (by weight) aqueous dispersions of the flour sulfates ranged from 91 to 93% based on 100% transmission for distilled water. At the same concentration, unmodified wheat flour had a clarity value of only 12%.

Preliminary evaluations of the suitability of sulfated wheat flour for a number of industrial applications are sufficiently promising to warrant further investigations of its utility as a flocculating agent, an oil-well drilling-mud additive, and a surface size for paper.

The present study represents part of a research program on the chemical modification of wheat flour to develop new nonfood industrial products such as sizing agents, adhesives, and flocculating agents. Little, if any, wheat flour is currently used for such products because its dispersibility in aqueous systems is too limited and its pastes lack the required uniformity and stability. In a previous phase of this program, dispersibility, paste uniformity, and stability of paste viscosity of flour were considerably improved by hydroxyethylation (5). Still higher dispersibility, as well as new levels of viscosity, was sought. Since relatively low levels of sulfation confer a high degree of dispersibility to starch, cellulose, and proteins, sulfation of flour appeared to be the best suited to achieve these objectives.

Highly dispersible sulfates of starch and a number of proteins have been prepared in good yields by employing tertiary-amine-sulfuric anhydride complexes as sulfating agents (1,2,8). Trimethylamine-sulfuric anhydride was used as the sulfating reagent in the present study

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because unlike other reagents (3,4,6,7), it reacts smoothly at 25°–60°C. in a slightly alkaline aqueous system. Relatively small amounts of the amine $-SO_3$ complex gave highly dispersible flour sulfates in good yields. The influence of time, temperature, pH, and the amount of reagent on the preparation and properties of flour sulfates is discussed.

Materials

The commercial hard red winter wheat flour used (Gloria Baker's Flour, Beardstown Mills) was unbleached, not malted, and contained 12–14% moisture and 12.8% protein. Trimethylamine-sulfur trioxide was prepared from trimethylamine and sulfuric anhydride according to the method of Wurzburg (8). The reference materials—pearl corn starch, methyl cellulose, hydroxyethylated corn starch, sodium cellulose sulfate, carboxymethyl cellulose, and reagents, sulfuric anhydride and trimethylamine—all came from commercial sources. The wheat starch employed (Hercules No. 120) was commercial, prime, and edible.

Experimental

The method employed in the sulfation of wheat flour with trimethylamine-sulfur trioxide was an adaptation of the procedure described by Wurzburg, Rutenberg, and Lawrence (8).

Typical Sulfation Procedure. Wheat flour (87.0 g., dry basis) was added to 125 g. of distilled water and the mixture stirred at room temperature for 15 minutes. Thirty-three grams of 3% (by weight) aqueous sodium hydroxide solution were added to the aqueous slurry under continuous stirring. After 15 minutes, 10 g. of trimethylamine-sulfur trioxide were added to the stirred alkaline mixture, and the reaction was allowed to proceed with stirring for 24 hours at room temperature in a closed system. At the end of this period the viscous reaction product was poured into a beaker; complete removal was achieved by rinsing the reaction vessel with 400 to 600 ml. of distilled water. The mixture was stirred until uniform, and the pH adjusted to 6.9 with dilute hydrochloric acid. The mixture was centrifuged, supernatant liquid was siphoned off, and the product was slurried in 300 ml. of absolute ethanol. The product was isolated from the alcoholic mixture by either centrifugation or filtration, washed twice with absolute ethanol, and dried to constant weight in a vacuum desiccator over phosphorus pentoxide. The dried product was ground in a Wiley Mill using a 40-mesh screen. Yield, 72 g. sulfur, 2.12 calcd. as weight percent $-SO_3H$, percent nitrogen, 0.42.

The sulfur and nitrogen analyses reported were determined by the

Micro-Carius and the Micro-Kjeldahl methods, respectively. The standard deviation for the sulfur analyses was 0.06 and for the nitrogen analyses 0.04.

Preparation of Sulfated Wheat Flour

Effects of time, temperature, catalyst (sodium hydroxide) concentration, and amount of sulfating agent employed on the extent of sulfation, as well as yield of product, are given in Table I. Sulfated corn and

TABLE I

EFFECT OF TIME, TEMPERATURE, CATALYST CONCENTRATION, AND AMOUNT OF SULFATING AGENT ON THE EXTENT OF SULFATION OF WHEAT FLOUR AND WHEAT OR CORN STARCHES[a]

SAMPLE	PRODUCT SULFATED	SULFATING AGENT	REACTION CONDITIONS		YIELD	SULFUR CALC'D. AS WEIGHT % -SO_3H
			Time	Temperature		
		g	*hours*	*°C*	*g (d.b.)*	
A	Wheat flour	5	24	25	71	1.97
B	Wheat flour	10	24	25	72	2.12
C	Wheat flour	15	24	25	73	3.41
D	Wheat flour	10	4	25	69	1.47
E	Wheat flour	10	12	25	69	1.90
F	Wheat flour	10	48	25	71	2.66
G	Wheat flour[b]	10	0.5	60–65	42	4.05
			23.5	25		
H	Wheat flour	10	24	25	68	4.60
I	Wheat starch	10	24	25	87	2.65
J	Corn starch	10	24	25	89	3.13

[a] In all preparations 87 g. flour (dry basis) were used with 125 g. water and 33 g. of aqueous sodium hydroxide solution (3% by weight), except for sample H where this solution was doubled (66 g.).
[b] Reaction mixture was heated at 60°–65°C. for 0.5 hour, then, allowed to react at 25°C. for 23.5 hours.

wheat starches are included in Table I for comparison.

Data on samples A, B, and C, Table I, show that the total sulfur content of the product increased with corresponding increases in the amount of sulfating agent used. However, the efficiency of trimethylamine-sulfur trioxide as a sulfating agent for wheat flour decreased from 51 to 34% as the amount of reagent was increased from 5 to 15 g.

The effect of time on the extent of sulfation is illustrated by samples D, E, B, and F, Table I. Using identical amounts of reactants but varying the reaction time resulted in corresponding increases in sulfur content. Time of reaction not only influences the extent of sulfation but also has a slight effect on product yield.

Heating the reaction mixture for 30 minutes at 60°–65°C. (sample G, Table I) increased the degree of sulfation achieved but also led to a much lower yield than was obtained in the reaction wholly carried out at 25°C. Because partial gelatinization of the flour occurred at

60°–65°C., workup and recovery of the product were difficult, and it was not further evaluated.

Doubling the alkali concentration of the reaction mixture (sample H, Table I) resulted in a lower yield of sulfated wheat flour. The loss in yield is probably due to (a) more extensive hydrolysis of the polymeric components in wheat flour to soluble materials and (b) gelatinization of some starch granules. The extent of sulfation was comparable to that achieved by heating the reaction mixture, but greater than that for products obtained from the same amount of sulfating agent and half the quantity of alkaline catalyst.

All the wheat flour sulfates were insoluble in cold water but soluble in cold dilute (0.5%) sodium hydroxide.

Evaluation of Sulfated Wheat Flour

Dispersibility. To ascertain what effect sulfating wheat flour with trimethylamine-sulfur trioxide had on improving the dispersibility of the parent substance, the percentage of material dispersed in hot water was determined for unmodified and sulfated wheat flour. Dispersibility was determined as follows: A 2.0-g. sample (dry basis) of material was transferred to a dry calibrated 250-ml. centrifuge bottle, followed by addition of 98 ml. of distilled water with gentle shaking. The mixture was mechanically stirred at approximately 526 r.p.m. for 30 minutes at 92°–100°C. The mixture was cooled to room temperature by immersing the bottle in cold water, followed by correcting the water level of the sample to its original volume, and stirring for 5 minutes without heating. The aqueous dispersion was centrifuged for 15 minutes at 2,500 r.p.m. Two 25-ml. aliquots of the supernatant liquid were transferred to tared evaporating dishes, the supernatant liquid was evaporated, and the residue dried to constant weight in a forced-draft oven at 100°–105°C. The dried residue was weighed, and the percent dispersible material was calculated as follows:

$$\frac{\text{Residue weight} \times 3.92 \times 100}{2} = \text{percent dispersibles}$$

The dispersibility of flour sulfates (Table II) ranged from 82 to 96%. It is evident, from a comparison of the percent dispersibles for aqueous systems of the unmodified and sulfated wheat flour, that the introduction of the hydrophilic sulfate group into flour with trimethylamine-sulfur trioxide greatly improves dispersibility. Further examination of the dispersibility of the sulfated wheat flours given in Table II reveals that time (samples E and B) and catalyst concentra-

TABLE II

EFFECT OF TIME AND CATALYST CONCENTRATION ON DISPERSIBILITY AND PASTE CLARITY OF AQUEOUS SYSTEMS OF SULFATED WHEAT FLOUR

WHEAT FLOUR	SAMPLE REFERENCE TO TABLE I	PERCENT DISPERSIBLES	PASTE CLARITY AFTER 24 HOURS		
			1%	5%	8%
Sulfated	E	96	90	48	20
Sulfated	B	82	93	47	24
Sulfated	H	92	91	46	32
Unmodified	..	11	12	3	2

tion (samples B and H) are preparative factors which influence the dispersibility of the product.

Clarity. The clarity (transparency) of aqueous systems of starch and wheat flour is important, because this property indicates the degree of molecular dispersion. Paste clarity was determined as follows: Weighed samples of products were dispersed in 20 ml. of distilled water in matched test tubes (Pyrex 9800, 18 by 150 mm.) by cooking and stirring for 30 minutes in a boiling-water bath followed by cooling for 1 hour in running tapwater. Water was added when necessary to compensate for its loss during heating, and the pastes were stored for 24 hours at 8°C. After the pastes had been allowed to reach room temperature, readings were made in a Coleman Junior Model 6A Spectrophotometer.[2] Paste clarity was reported as percentage transmission of light at 650 mμ based on 100% transmission for distilled water.

The effect of concentration on the clarity of aqueous systems of sulfated wheat flour is shown in Table II. Although only 24-hour values are given, no change in paste clarity of the sulfated materials was apparent after they had stood at room temperature for 72 and 168 hours respectively – thus indicating their stability.

Extending the reaction time had a tendency to improve the paste clarity of the sulfated wheat flour, as shown by samples E (12 hours) and B (24 hours), Table II. Increasing the alkali content of the reaction mixture (sample H) improved paste clarity at concentrations above 5%.

Pasting Properties

The changes in consistency that occur during the pasting, cooking, and cooling of aqueous systems of sulfated wheat flour, sulfated wheat and corn starches, and unmodified wheat flour are shown in Table III. These properties were determined in a Brabender Amylograph Viscograph, Model No. 209, having a cup speed of 75 r.p.m., a uniform

[2] Mention of firm names or trade products does not imply that they are endorsed by the Department of Agriculture over other firms or similar products not mentioned.

TABLE III

PASTING CHARACTERISTICS OF 4-PERCENT (BY WEIGHT) AQUEOUS DISPERSIONS OF WHEAT FLOUR SULFATES, CORN AND WHEAT STARCH SULFATES, AND UNMODIFIED WHEAT FLOUR AS DETERMINED BY A BRABENDER AMYLOGRAPH VISCOGRAPH

SAMPLE AND REFERENCE TO TABLE I		SULFATING AGENT	REACTION TIME	GELATINIZATION TEMP. RANGE	VISCOSITY (CP)			
					Hot Max.	Hot Min. 92°C.	At 55°C.	Setback, 25°C.
		g	*hours*	*°C*				
Sulf. wht. fl.	A	5	24	50–65	825	198	544	808
Sulf. wht. fl.	C	15	24	43–69	1,353	181	412	627
Sulf. wht. fl.	D	10	4	53–68	961	190	537	730
Sulf. wht. fl.	E	10	12	50–67	1,366	267	759	1,116
Sulf. wht. fl.	B	10	24	54–69	990	188	561	775
Sulf. wht. fl.	F	10	48	31–58	1,576	214	660	937
Sulf. wht. fl.	H	10	24	25–50	1,887	306	730	1,347
Unmod. wht. fl.	..	..	..	25–90	17	17	18	74
Sulf. wht. starch	I	10	24	40–60	1,023	237	589	858
Sulf. corn starch	J	10	24	55–62	1,551	198	346	602

heating rate of 1.5°C. rise in temperature per minute, and the same cooling rate. Four percent aqueous dispersions of wheat flour sulfates were used, because higher concentrations were too viscous to be recorded within the range of the Brabender Amylograph Viscograph.

In the preparation of wheat flour sulfates, increasing the amount of sulfating agent from 5 to 15 g. gave a product with higher hot maximum viscosity but with lower setback viscosity. Gradual lowering of the gelatinization temperature of the wheat flour sulfates occurred as the reaction time was extended from 4 to 48 hours; this effect was accompanied by an increase in the hot maximum viscosities of the sulfated wheat flours.

A twofold increase in alkali content of the reaction mixture (compare samples B and H) yielded a sulfated wheat flour having a low initial gelatinization temperature and exhibiting the highest hot maximum and setback viscosities of any product obtained in this investigation. It is doubtful that these changes in pasting properties can be attributed to the higher $-SO_3H$ content, because the pasting properties of sample C with an $-SO_3H$ content of 3.41% did not differ materially from those of sample A where the content was only 1.97%.

A comparison of the pasting properties of unmodified flour with those of sulfated flour shows that sulfation greatly increases paste viscosity, reduces the time and temperature required for gelatinization, and narrows the gelatinization temperature range considerably.

Brookfield Paste Viscosity. Two-percent (by weight) aqueous dispersions of sulfated wheat flours from the 4-, 12-, and 48-hour reactions, respectively, unmodified wheat flour, or starch, and hydroxyethylated

corn starch were prepared by pasting samples in water at 90° C. for 30 minutes and allowing the cooked pastes to cool to room temperature. Because carboxymethyl cellulose, sodium cellulose sulfate, and methyl cellulose are cold water-soluble, their dispersions were prepared without heating. All dispersions were equilibrated to 25°C. in a constant-temperature bath before measurements were made.

A Brookfield Synchro-Lectric Viscometer, Model LVF, having four speeds (6, 12, 30, and 60 r.p.m.) was used to determine the apparent viscosity of the aqueous dispersions at 25°C. and 30 r.p.m. (Table IV).

TABLE IV

COMPARATIVE BROOKFIELD VISCOSITIES OF 2-PERCENT (BY WEIGHT) AQUEOUS DISPERSIONS OF SULFATED WHEAT FLOUR AND COMMERCIAL DERIVATIVES OF CELLULOSE AND STARCH AT 25°C. AND 30 R.P.M.

SAMPLE	SAMPLE REFERENCE TO TABLE I	VISCOSITY	pH
		cp	
Sulfated wheat flour	D	4,246	6.5
Sulfated wheat flour	E	4,360	6.5
Sulfated wheat flour	F	900	5.8
Carboxymethyl cellulose (medium viscosity type)	..	750	6.9
Sodium cellulose sulfate	..	229	6.8
Methyl cellulose (400 centipoises — medium viscosity type)	..	368	8.0
Hydroxyethylated corn starch	..	155	7.0
Unmodified wheat flour	..	30	6.1
Unmodified wheat starch	..	16	7.3

Examination of data in Table IV shows that wheat flour sulfates exhibited considerably higher viscosities at 25°C. than a number of representative commercial gums and unmodified materials. In a comparison of the viscosities of the wheat flour sulfates, the decrease in viscosity shown by the 48-hour product (sample F) suggests that time-of-reaction was a contributing factor in promoting partial hydrolysis of the polymeric components of wheat flour under the influence of an alkaline medium.

Isolation and Properties of Crude Wheat Flour Sulfate

Nitrogen analysis of the flour sulfates thus far discussed showed that approximately 80–90% of the protein originally present in the flour was lost in working up the crude reaction mixture. The question arose whether this loss could be significantly reduced without seriously affecting properties of the product by eliminating some purification steps. Considerable economy would be realized by elimination of

alcohol washing. To pursue this investigation, wheat flour was sulfated under conditions identical to those given for a typical preparation in the "Materials and Methods" section. In the isolation, however, instead of washing with alcohol, the crude solid mass obtained after centrifugation and removal of supernatant liquid was diluted with water to give a 10% slurry and then dried on hot rolls. The temperature of the rolls was 121°C.; the speed of the 6-in. rolls was 4 r.p.m.; and the clearance was 0.006 in. The product was obtained in a 93% weight yield based on the starting weight of dry flour and had the following properties:

Physical state: Off-white to ivory-colored solid	
Nitrogen content:	1.23%
Dispersibility:	98%
Clarity of 2% paste after 24 hours:	14%
Sulfur content, calcd. as wt. percent $-SO_3H$:	4.07

Pasting characteristics of 4% aqueous slurry	
Gelatinization temperature range:	25°–61°C.
Hot maximum viscosity (61°C.):	768 cp.
Hot minimum viscosity:	65 cp.
Viscosity at 55°C.:	325 cp.
Setback viscosity at 25°C.:	537 cp.

Nitrogen content of the crude product showed that protein loss was reduced from the 80 to 90% level previously experienced in purification to 44%. Paste clarity of the crude product was considerably less and its paste viscosity somewhat lower than for the purified sulfates. However, it is believed that the protein content, paste clarity, and paste viscosity can be considerably improved by minor changes in processing and that the crude products will prove to be as useful for most purposes as the purified materials.

Evaluation of sulfated wheat flour in several potential areas of application is under way, and preliminary results are sufficiently promising to warrant further investigation of its utility as a flocculating agent, an oil-well drilling-mud additive, and a surface size for paper.

The utility of other organo-sulfuric anhydride complexes as sulfating agents for flour is also being investigated and will be reported in subsequent papers.

Summary and Conclusions

Ungelatinized sulfates of hard red winter wheat flour with sulfur contents ranging from 1.47 to 4.6 weight percent, calculated as $-SO_3H$, were prepared in 80–90% weight yield by treatment at 25°C. with nominal amounts of trimethylamine-sulfur trioxide in an aqueous system catalyzed by sodium hydroxide. The extent of sulfation was influenced by reaction time, temperature, concentration of catalyst

(NaOH), and amount of sulfating agent employed.

The dried, ground, wheat flour sulfate was practically colorless; it was free-flowing; and it had a slight odor of trimethylamine. Wheat flour sulfates are insoluble in cold water but soluble in dilute (0.5%) aqueous sodium hydroxide.

Aqueous dispersions of wheat flour sulfates when heat-gelatinized exhibited high viscosity, excellent clarity, and a high degree of dispersibility in marked contrast to comparable dispersions of the parent wheat flour. Pasting studies revealed that 1) high initial hot maximum and 2) high setback viscosities were both general for wheat flour sulfates. All the washed wheat flour sulfates were low in nitrogen. On the basis of nitrogen analyses, 80–90% of the protein was removed, indicating that during sulfation soluble protein materials were produced and subsequently removed during the workup of the sulfated product. Crude wheat flour sulfate that was not purified by washing procedures retained 56% of the flour protein and was obtained in an almost quantitative yield. Except for poor clarity, over-all properties of the crude product were comparable to those of the purified wheat flour sulfate.

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