

**NOTE ON THE PREPARATION AND USE OF
POLY-2-VINYLPYRIDINE-SULFUR TRIOXIDE
AS A SULFATING AGENT FOR STARCH¹**

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Previous studies (2) on the sulfation of wheat flour and of corn and wheat starches revealed that trimethylamine-sulfur trioxide was an effective sulfating agent. However, these sulfated products had an

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amine odor that could not be completely removed by practical methods of extraction, evaporation, or washing. To overcome the odor problem, studies on the development of a sulfating agent derived from an odorless, nonvolatile, polymeric amine and sulfuric anhydride were undertaken. For this purpose poly-2-vinylpyridine was reacted with sulfuric anhydride, and the resulting sulfur trioxide adduct investigated as a sulfating agent for starch. Poly-2-vinylpyridine-sulfur trioxide proved an effective sulfating agent for starch and met the requirements of water-solubility and lack of odor. The residual polyamine was compatible with the starch sulfate and did not have to be removed from the reaction medium. The present paper reports the preparation and use of poly-2-vinylpyridine-sulfur trioxide as a novel sulfating agent for unmodified and modified starches.

Materials and Methods

Polymerization of 2-Vinylpyridine. Crude 2-vinylpyridine (Reilly Tar and Chemical Corp.)² was fractionally distilled twice under reduced pressure and a nitrogen atmosphere. The final constant boiling fraction (61.5°C. at 23 mm.) was polymerized for 24 hours at 53°–55°C. under nitrogen following essentially the procedure described by Harmon (1). Poly-2-vinylpyridine was obtained in good yield. Elemental analyses on both monomer and polymer were in good agreement with theoretical values.

Preparation of Poly-2-Vinylpyridine-Sulfur Trioxide. Purified 1,2-dichloroethane (1,400 ml.) was placed in a 3-liter, 3-necked, round-bottomed flask equipped with a True-Bore stirring assembly, a pressurized dropping funnel protected by a calcium chloride drying tube, and a thermometer housed in a mercury well. Poly-2-vinylpyridine (80 g.) was added to the solvent with agitation until solution was effected. The amber-colored solution was cooled externally by a solid carbon dioxide bath to 20°C., followed by dropwise addition of DuPont's Stabilized liquid sulfur trioxide (60 g.) under continuous stirring. The rate of addition of the sulfur trioxide was controlled to maintain a reaction temperature between 18° and 22°C. Upon complete addition of the sulfur trioxide the reaction mixture was stirred for an hour at 20°C. The crude reaction mixture was blended in a large Waring Blendor; the product was collected on a canvas filter and then washed by blending in cold (10°–15°C.) purified 1,2-dichloro-

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

ethane. The washed product was collected, sucked as dry as possible with a rubber dam, reslurried in diethyl ether to remove any residual reaction solvent, isolated again, and dried in a vacuum desiccator over sulfuric acid. Yield was 132 g. The product was soluble in water, mineral acids, glycerol, ethylene glycol, dimethylsulfoxide, and pyridine; insoluble in aqueous alkalis, alcohols, acetic acid, dioxane, hydrocarbons, diethyl ether, and chlorinated solvents.

Analysis: Calc'd for $(C_7H_7NSO_3)_x$: S, 17.28. Found: S, 17.26.

Typical Starch Sulfation Procedure. Hypochlorite-oxidized corn starch (52.5 g.) containing 10.5% moisture was stirred and heated in 947.5 g. of distilled water to form a gelatinous paste. The paste was stirred and heated for an additional 30-minute period at 90°–95°C. With continuous stirring the paste was cooled to 40°C. Poly-2-vinylpyridine-sulfur trioxide (6.0 g.) was added, and the mixture was stirred and heated at 50°–51°C. for 1 hour in a closed system. The reaction mixture was cooled to 40°C., then poured into stirred alcohol to precipitate the starch sulfate. After settling, the heavy, sticky product was collected, then partially dehydrated by slurring in a minimum of absolute alcohol. The product was again collected by filtration and partially dried in a vacuum desiccator over phosphorus pentoxide. The starch sulfate was finally dried in a vacuum oven at 55°C. for 18 hours. The brittle material was ground in a Wiley Mill with a 40-mesh screen. Yield was 50.3 g. (dry basis). Percent sulfur calculated as $-SO_3H$ was 1.79.

Results

Poly-2-vinylpyridine-sulfur trioxide, when employed as a sulfating agent, readily sulfated gelatinized hypochlorite-oxidized corn starch and commercial unmodified corn starch in an aqueous medium in a closed system. Starch sulfates ranging in sulfur content from 0.76 to 3.29% calculated as weight percent $-SO_3H$ in 90–95% yield resulted when 3 to 12 g. of sulfating agent were reacted with 50 g. of dry starch. Nearly maximum $-SO_3H$ content was achieved in 1-hour reaction time for a given temperature and concentration of sulfating agent. Poly-2-vinylpyridine-sulfur trioxide was not as effective a sulfating agent for granular starches as it was for gelatinized. Perhaps the polymeric sulfating agent does not effectively penetrate the starch granules. Paste viscosities of the starch sulfates were comparable to those of dextrans used for envelope gums. Aqueous dispersions of starch sulfates gave quick-setting pastes that exhibited unusual tackiness and adhesive characteristics.

Literature Cited

1. HARMON, J. Polymerization of vinylpyridines. U.S. Patent No. 2,491,472 (Dec. 20, 1949).
2. SMITH, H. E., RUSSELL, C. R., and RIST, C. E. Preparation and properties of sulfated wheat flour. *Cereal Chem.* **39**: 273-281 (1962).

