

## Insoluble Starch Xanthate: Use in Heavy Metal Removal

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### Synopsis

Water-insoluble starch xanthates were prepared by xanthation of highly crosslinked starches under various conditions. After isolation of the products by solvent dehydration, freeze drying, or spray drying, their properties were determined. These products were very effective in removing heavy metals from water.

### INTRODUCTION

It has been previously shown that water-soluble starch xanthates in combination with cationic polymers form polyelectrolyte complexes<sup>1-3</sup> that effectively remove heavy metals from wastewater. Research along these lines has continued with the goal of eliminating the expensive cationic polymer to give a more economical method of heavy metal removal. This paper reports the xanthation of a highly crosslinked starch to give a water-insoluble product that is effective in removing heavy metals from water without the need for a cationic polymer.

Most starches used in this work were crosslinked to various degrees with epichlorohydrin. Products which exhibited little or no swelling in water in the presence of base were selected for xanthation.

Several different xanthation conditions and work-up schemes were evaluated to obtain preliminary guidelines for the development of a potential commercial process for making insoluble starch xanthate.

### EXPERIMENTAL

#### Xanthation of Crosslinked Starches

A highly crosslinked starch (53-91E, Vulca 100, 10136-1 from Table I) (35.4 g) was slurried in water (225 ml), sodium hydroxide (8 g) in water (100 ml) was added, and the mixture was stirred 30 min. Then carbon disulfide (5 ml) was added and the mixture was stirred 16 hr at 25°C. The slurry was filtered through a coarse fritted-glass funnel and the solid was washed successively with water (75 ml), several portions of acetone (500 ml total), and ether (100 ml). After drying in a vacuum oven at 25°C for 2 hr, the pale-yellow solid was stored at 0° in a closed container. Weights and volumes of reactants and analysis of the final product for several preparations are found in Table II.

TABLE I  
Degree of Swelling of Crosslinked Starches<sup>a</sup>

| Starch                 | Hot water, <sup>b</sup><br>cm | Cold caustic, <sup>c</sup><br>cm | Hot caustic, <sup>d</sup><br>cm |
|------------------------|-------------------------------|----------------------------------|---------------------------------|
| Vulca 30 <sup>e</sup>  | 4.7                           | 6.7                              | 8.5                             |
| Vulca 60 <sup>e</sup>  | 2.7                           | 4.1                              | 4.1                             |
| Vulca 100 <sup>e</sup> | 1.2                           | 1.6                              | 1.6                             |
| 53-91E <sup>f</sup>    | 1.2                           | 1.3                              | 1.3                             |
| 53-91P <sup>f</sup>    | 2.0                           | 2.4                              | 3.5                             |
| 10136-1 <sup>g</sup>   | 1.2                           | 1.6                              | 1.6                             |

<sup>a</sup> Sample (0.5 g) in water (15 ml) in test tube (1.5 cm × 15 cm); height of water, 9.5 cm. Sample height, originally 1.2 cm.

<sup>b</sup> Sample heated in 90° hot-water bath 20 min, then cooled to room temperature. Values indicate height of starch in cm.

<sup>c</sup> Sodium hydroxide (0.15 g) dissolved in each sample.

<sup>d</sup> Samples from (c) heated as in (b).

<sup>e</sup> National Starch and Chemical Corp., Plainfield, New Jersey.

<sup>f</sup> The Hubinger Starch Co., Keokuk, Iowa.

<sup>g</sup> NRRL experimental product.

TABLE II  
Preparation of Insoluble Starch Xanthate

| Starch used <sup>a</sup> | Starch wt, g | Base used, <sup>b</sup> g | Carbon disulfide, <sup>c</sup> ml | Product wt, g | % S (as is) | % Ash, <sup>d</sup> d.b. | % H <sub>2</sub> O <sup>e</sup> |
|--------------------------|--------------|---------------------------|-----------------------------------|---------------|-------------|--------------------------|---------------------------------|
| 53-91E                   | 35.4         | NaOH, 8                   | 5                                 | 43.0          | 5.46        | 15.7                     | 12.2                            |
|                          | 35.4         | NaOH, 8                   | 10                                | 41.0          | 6.82        | 11.7                     | 9.6                             |
|                          | 35.4         | NaOH, 16                  | 5                                 | 48.4          | 6.43        | 22.1                     | 15.6                            |
|                          | 35.4         | NaOH, 16                  | 10                                | 50.0          | 9.44        | 22.2                     | 14.9                            |
|                          | 70.8         | NaOH, 32                  | 10                                | 95.6          | 5.59        | 19.9                     | 16.3                            |
|                          | 35.4         | KOH, 11.2                 | 5                                 | 41.4          | 4.98        | 12.6                     | 6.1                             |
|                          | 35.4         | KOH, 22.4                 | 10                                | 48.1          | 10.20       | 15.9                     | 9.8                             |
|                          | 10.0         | KOH, 50                   | 25                                | 16.0          | 17.32       | 30.3                     | 8.6                             |
| Vulca 100                | 35.4         | NaOH, 8                   | 5                                 | 43.1          | 4.90        | —                        | —                               |
|                          | 35.4         | KOH, 22.4                 | 10                                | 49.0          | 10.84       | 21.5                     | 9.6                             |
| Vulca 60                 | 35.4         | KOH, 22.4                 | 10                                | 48.9          | 10.48       | 24.8                     | 8.5                             |
| 53-91P                   | 35.4         | KOH, 22.4                 | 10                                | 51.8          | 10.13       | 25.9                     | 11.9                            |
| 10136-1                  | 177.0        | NaOH, 40                  | 25                                | 225.0         | 8.37        | 14.9                     | 15.1                            |

<sup>a</sup> Crosslinked starch: 53-91E (epichlorohydrin) (The Hubinger Company, Keokuk, Iowa), 9.1% H<sub>2</sub>O; 53-91P (phosphorus oxychloride) (The Hubinger Company, Keokuk, Iowa), 10.7% H<sub>2</sub>O; Vulca 100 and Vulca 60 (epichlorohydrin) (National Starch and Chemical Corp., Plainfield, New Jersey), 10.9% and 11.0% H<sub>2</sub>O, respectively; and 10136-1 (epichlorohydrin) (NRRL experimental product), 9.5% H<sub>2</sub>O.

<sup>b</sup> 8 g NaOH ~ 0.2 mole; 11.2 g KOH ~ 0.2 mole.

<sup>c</sup> 5 ml CS<sub>2</sub> ~ 0.08 mole.

<sup>d</sup> % Ash includes metal ion of xanthate and bound alkali in product.

<sup>e</sup> % H<sub>2</sub>O is uncorrected for xanthate decomposition that occurred during moisture analysis which was run at room temperature under vacuum for 2-3 hr.

### Short-Time (1- or 4-hr) Xanthation of Crosslinked Starch

The xanthations were performed as previously described; however, the reactions were terminated after 1 and 4 hr. The product analysis is shown in Table III.

TABLE III  
Short Time (1- or 4-hr) Xanthation of Crosslinked Starch

| Time, hr | Starch used <sup>a</sup> | Starch wt, g | Base used, <sup>b</sup> g | Carbon disulfide, <sup>c</sup> ml | Product wt, g | % S (as is) | % Ash, <sup>d</sup> d.b. | % H <sub>2</sub> O |
|----------|--------------------------|--------------|---------------------------|-----------------------------------|---------------|-------------|--------------------------|--------------------|
| 1        | 53-91E                   | 100          | NaOH, 45                  | 15                                | 133.5         | 6.55        | 13.4                     | 19.1               |
| 4        | 53-91E                   | 35.4         | NaOH, 16                  | 5                                 | 48.4          | 6.57        | 16.7                     | 14.3               |
| 4        | 53-91E                   | 100          | NaOH, 45                  | 15                                | 132.0         | 6.52        | 9.7                      | 14.0               |

<sup>a</sup> Crosslinked starch: 53-91E (epichlorohydrin) (The Hubinger Company, Keokuk, Iowa), 9.1% H<sub>2</sub>O.

<sup>b,c,d,e</sup> Same as in Table II.

TABLE IV  
25% Solids Xanthation of Crosslinked Starch

| Starch used <sup>a</sup> | Work-up                            | Product wt, g | % S (as is) | % Ash, <sup>b</sup> d.b. | % H <sub>2</sub> O <sup>c</sup> |
|--------------------------|------------------------------------|---------------|-------------|--------------------------|---------------------------------|
| 53-91E                   | solvent only <sup>d</sup>          | 53.0          | 5.40        | 34.3                     | 18.5                            |
| 53-91E                   | centrifuge-solvent <sup>e</sup>    | 42.8          | 6.46        | 12.8                     | 8.6                             |
| 53-91E                   | centrifuge-freeze dry <sup>f</sup> | 42.0          | 8.61        | 9.2                      | 6.6                             |

<sup>a</sup> Same as footnote (a) in Table II.

<sup>b</sup> Same as footnote (d) in Table II.

<sup>c</sup> Same as footnote (e) in Table II.

<sup>d</sup> Usual acetone-ether wash followed by vacuum oven drying at 25°C.

<sup>e</sup> Centrifuged four times with water (800 ml total) wash; then (d).

<sup>f</sup> Centrifuged four times with water (800 ml total) wash; then freeze dried in 150 ml water.

### 25% Solids Xanthation of Crosslinked Starch

Crosslinked starch (53-91E, 35.4 g) was slurried in water (100 ml), and sodium hydroxide (16 g) in water (31 ml) was added. Carbon disulfide (5 ml) was added and the reaction mixture was stirred for 16 hr at 25°C. The mixture was filtered and worked up by solvent washing as previously described. Other work-up procedures (e.g., centrifuging, then solvent washing and centrifuging, then freeze drying) were also investigated (Table IV).

### Reuse of Mother Liquor in Xanthation of Crosslinked Starch

Crosslinked starch (53-91E, 100 g) was slurried in water (350 ml) and sodium hydroxide (45 g) in water (50 ml) was added. Carbon disulfide (15 ml) was added and the mixture was stirred for 16 hr at 25°C. The mixture was filtered and washed with a small volume of water to give 400 ml of mother liquor, which was saved for subsequent xanthations. The solid was washed with acetone and ether and was dried as previously described. In Table V, the results are shown for a series of four xanthations in which the mother liquor derived from the previous xanthation was used.

### One-Step Crosslinking and Xanthation of Starch

Commercial corn starch (100 g, 10% H<sub>2</sub>O) was slurried in water (150 ml) containing sodium chloride (1.5 g) and epichlorohydrin (5.5 ml). To this slurry was added potassium hydroxide (6 g) in water (40 ml) slowly over 30 min. The

TABLE V  
Reuse of Mother Liquor in Xanthation of Crosslinked Starch

| Xanthation no. <sup>a</sup> | Base, g         | Product wt, g | % S (as is) | % Ash, <sup>b</sup> d.b. | % H <sub>2</sub> O <sup>c</sup> |
|-----------------------------|-----------------|---------------|-------------|--------------------------|---------------------------------|
| 1                           | 48              | 128.3         | 6.06        | 16.6                     | 13.1                            |
| 2                           | 24 <sup>d</sup> | 127.5         | 4.20        | 14.0                     | 14.1                            |
| 3                           | 12 <sup>d</sup> | 119.3         | 4.56        | 9.1                      | 11.3                            |
| 4                           | 12 <sup>d</sup> | 119.2         | 4.44        | 8.8                      | 11.2                            |

<sup>a</sup> Crosslinked starch (53-91E, 100 g) and carbon disulfide (15 ml) were used for each xanthation.

<sup>b</sup> Same as footnote (d) in Table II.

<sup>c</sup> Same as footnote (e) in Table II.

<sup>d</sup> Weight of additional sodium hydroxide dissolved in mother liquor (400 ml) from the previous xanthation.

slurry was warmed to 50°C and then cooled to room temperature. Water (50 ml) and epichlorohydrin (2 ml) were added and the mixture was stirred for 16 hr. The suspension, now containing highly crosslinked starch, was treated with sodium hydroxide (48 g) in water (250 ml). Carbon disulfide (15 ml) was added near the bottom of the beaker and the mixture was stirred for 16 hr. The mixture was filtered and was washed with water (100 ml), acetone (750 ml), and ether (200 ml). After drying for 2 hr under vacuum, the product was analyzed. Yield: 132.2 g; S, 5.56%; H<sub>2</sub>O, 11.4%; ash, 14.3%.

The reaction was repeated on 506 g starch but without the heating step, the additional water, and epichlorohydrin during crosslinking. Yield: 657 g; S, 7.26%; H<sub>2</sub>O, 18.1%; ash, 19.5%.

### Spray-Dried Product

Crosslinked starch (53-91E, 177 g) was slurried in water (655 ml), and sodium hydroxide (40 g) in water (100 ml) was added. Carbon disulfide (25 ml) was added below the liquid surface and the mixture was stirred for 16 hr. The mixture was centrifuged and washed four times with water (1600 ml total) in centrifuge bottles. The product was suspended in water (500 ml) to give a final volume of 1000 ml. This suspension was stirred and pumped into a NIRO portable spray drier (Copenhagen, Denmark) at a rate of 3 l./hr (spindle speed, 35,000 rpm; inlet temperature, 260°C; and outlet temperature, 118°C). Yield: 190 g; S, 8.02%; H<sub>2</sub>O, 3.0%; ash, 11.6%.

### Insoluble Starch Xanthide

Insoluble starch xanthate was prepared as previously described under reuse of mother liquor. Before filtration, the reaction mixture was treated successively with glacial acetic acid (20 ml), sodium nitrite (28.5 g/50 ml water), and 6*N* HCl (250 ml). The mixture was stirred for 30 min, and the final pH was 3.8. The starch xanthide was filtered, washed with water (400 ml), acetone (750 ml), and ether (400 ml), and dried in a vacuum oven at room temperature for 5 hr. Yield: 110.8 g; S, 3.57%; H<sub>2</sub>O, 6.7%; ash, 0.9%.

### Insoluble Calcium Starch Xanthate

Insoluble sodium starch xanthate was prepared as previously described under reuse of mother liquor. After filtration, the product was washed with water

(200 ml) and a solution (200 ml) of calcium chloride (20 g). Following the usual wash with acetone and ether, the product was dried for 4 hr in a vacuum oven. Yield: 127 g; S, 4.87%; H<sub>2</sub>O, 11.9%; ash, 7.2%.

### Insoluble Magnesium Starch Xanthate

The same procedure was used as for the preparation of the calcium salt, except that magnesium chloride hexahydrate (40 g) was substituted for the calcium chloride. Yield: 134.5 g; S, 4.66%; H<sub>2</sub>O, 13.3%; ash, 10.7%.

## RESULTS AND DISCUSSION

The main purpose in forming this new starch xanthate was to have a product which would not swell in water but which would remove heavy metals from wastewater. Initially, several commercial and experimental crosslinked starches were evaluated to see which samples were the most highly crosslinked. The higher degree of crosslinking aids in the product's preparation and its use for removing heavy metals because of its ease of filtration. The extent of crosslinking was determined by the amount of swelling of each sample in cold and hot water. Since caustic would be used in the xanthation step, the extent of swelling was also determined in the presence of base (Table I). It was experimentally determined that three starch samples (Vulca 100, 53-91E, and 10136-1) were the most highly crosslinked; and, therefore, they were used in further studies.

Several preparations of insoluble starch xanthate were made to evaluate the properties of the different products (Table II). Various combinations of base and carbon disulfide gave different degrees of substitution to the products; however, the products were all effective in heavy metal removal.

Several other preparations were also made to determine optimal conditions for preparing insoluble starch xanthate on a large-scale basis. Three preparations of insoluble starch xanthate were made using a 1- or 4-hr reaction time instead of the more convenient 16-hr reaction time. The products obtained were as effective as those obtained utilizing longer reaction times (Table III). When the solids concentration was increased from 10% to 25%, similar products were obtained (Table IV). Also in this investigation several work-up methods were evaluated. We compared water washing on a filter followed by solvent drying; water washing with centrifugation, followed by solvent drying; and water washing with centrifugation, followed by freeze drying. The only real difference with these washing treatments was the loss of base associated with the products when more water was used during centrifugation. This loss of base also accounts for the increase in per cent sulfur of these products.

Since a considerable quantity of base remains in the filtrate and since large quantities of water would be required in large-scale production, the reuse of the mother liquor in subsequent xanthations was evaluated. Less base was used in each subsequent xanthation; and from the product analysis (Table V), it can be seen that a slightly less xanthated product was obtained. There was also a considerable decrease in the per cent ash, which is an indirect measure of the base still associated with the product. Therefore, if the mother liquor is to be reused, sufficient base should be added to bring the base concentration up to that used in the initial xanthation. The effectiveness of copper removal from water when comparing products 1 and 4 in Table V was good (Table VI).

TABLE VI  
Copper(II) Removal from Water with Mother Liquor Reuse Starch Xanthates

| Starch xanthate | Xanthate wt, g | [Cu], <sup>a</sup> $\mu\text{g}/\text{l}$ . | Initial pH | 2-Hr pH <sup>b</sup> | Residual [Cu], <sup>c</sup> $\mu\text{g}/\text{l}$ |
|-----------------|----------------|---|------------|----------------------|--|
| 1               | 0.0554         | 31,770                                      | 3.0        | 8.7                  | 11   |
| 4               | 0.0515         | 31,770                                      | 3.0        | 7.4                  | 11   |

<sup>a</sup> 50-ml solution.

<sup>b</sup> Stir 2 hr before filtering through a medium fritted-glass filter.

<sup>c</sup> Determined using a Varian Techtron AA120 spectrophotometer.

Since a basic medium is used for both crosslinking and xanthation, we investigated preparation of the xanthate without isolation of the crosslinked intermediate. After the starch had been crosslinked, additional base and then carbon disulfide were added. The products obtained were similar to those obtained in a separate two-step reaction.

The stability of insoluble starch xanthate samples varied considerably depending upon how the samples were worked up and stored. All samples that were stored at 0°C for eight months remained completely effective. Samples that were stored at room temperature decomposed slightly to give volatile sulfur-containing products which had a strong odor. The resulting starch products lost their effectiveness to remove heavy metals. Samples which remained yellow in color and had no perceptible odor remained effective for metal removal.

Several approaches were investigated to prepare products which would have room-temperature stability. Spray drying reduced the moisture content to 3%, and such a product was stable at room temperature for several months. Vacuum oven drying at temperatures of 30–50°C for several hours yielded products with 7–10% moisture. These products showed some decomposition when left at room temperature, and thus they were less effective for metal removal. Moreover, conversion of insoluble starch xanthate into insoluble starch xanthide with sodium nitrite did yield a product stable at room temperature. This product, however, was only effective in heavy metal removal when the pH of the solution was adjusted above 7 which leads to disruption of the xanthide linkage and partial regeneration of the active xanthate form.

Conversion of the insoluble sodium starch xanthate to either the calcium or magnesium form was accomplished by simply washing the product with the appropriate chloride salt. Calcium, magnesium, and sodium analyses of these products showed that this exchange procedure was 99% effective. The magnesium insoluble starch xanthate appeared to have good room-temperature stability for several months and was very effective in metal removal. The calcium insoluble starch xanthate was more stable than the sodium form but there was enough decomposition to render it ineffective in metal removal.

Insoluble starch xanthate could decompose to give nonvolatile sulfur compounds and show little loss in sulfur content. The samples were tested periodically for apparent stability by evaluating their effectiveness to remove copper from solution. Since copper was effectively removed with the same amount of insoluble starch xanthate stored at 0° or at room temperature with a moisture content of <3%, it was assumed there was little decomposition (Table VII). Samples which decomposed always gave a pink filtrate containing a high concen-

TABLE VII  
Apparent Stability of Insoluble Starch Xanthate-Copper(II) Removal from Water

| Product age, <sup>a</sup><br>weeks | Xanthate wt, <sup>b</sup><br>g | Residual<br>[Cu], <sup>c</sup> µg/l. |
|------------------------------------|--------------------------------|--------------------------------------|
| 1                                  | 0.0544                         | 14                                   |
| 1                                  | 0.0495                         | 12                                   |
| 2                                  | 0.0522                         | 12                                   |
| 10                                 | 0.0459                         | 39                                   |
| 23                                 | 0.0491                         | 25                                   |
| 43                                 | 0.0516                         | 31                                   |

<sup>a</sup> Sample no. 3 in Table II.

<sup>b</sup> 50-ml Solutions containing 31,770 µg Cu/l. Stir 2 hr before filtering through a medium fritted-glass filter.

<sup>c</sup> Determined using a Varian Techtron AA120 spectrophotometer.

TABLE VIII  
Removal of Heavy Metals from Water with Insoluble Starch Xanthate<sup>a</sup>

| Metal            | Initial<br>concn., <sup>b</sup><br>µg/l. | Initial<br>pH | 2-Hr<br>pH <sup>c</sup> | Residual<br>metal, <sup>b</sup><br>µg/l. | Illinois<br>discharge<br>limit, <sup>c</sup><br>µg/l. |
|------------------|--|---------------|-------------------------|--|---|
| Cu <sup>+2</sup> | 31,770                                   | 3.4           | 6.4                     | 7  | 20  |
| Ni <sup>+2</sup> | 29,350                                   | 3.2           | 7.7                     | 19                                       | 1,000   |
| Cd <sup>+2</sup> | 56,200                                   | 3.0           | 6.8                     | 9  | 50  |
| Pb <sup>+2</sup> | 103,600                                  | 3.1           | 7.3                     | 25                                       | 100   |
| Cr <sup>+3</sup> | 26,000                                   | 3.2           | 6.5                     | 3  | 1,000   |
| Ag <sup>+</sup>  | 53,940                                   | 3.1           | 7.2                     | 245                                      | 5   |
| Zn <sup>+2</sup> | 32,690                                   | 3.1           | 7.5                     | 46                                       | 1,000   |
| Fe <sup>+2</sup> | 27,920                                   | 3.0           | 6.4                     | 0  | 1,000   |
| Mn <sup>+2</sup> | 27,470                                   | 3.3           | 9.0                     | 1,628                                    | 1,000   |
| Hg <sup>+2</sup> | 100,000                                  | 3.1           | 4.2                     | 3  | 0.5   |

<sup>a</sup> Product no. 3 of Table II was used. Weight ranged from 0.0436 g to 0.0762 g/50-ml sample.

<sup>b</sup> 50-ml Sample.

<sup>c</sup> Stir solution 2 hr before filtering through a medium fritted-glass filter.

<sup>d</sup> Determined using a Varian Techtron AA120 spectrophotometer.

<sup>e</sup> State of Illinois discharge limits for public and food processing waters (Illinois Pollution Control Board, Newsletter No. 44, p. 7, March 1972).

tration of copper, and this suggested that low molecular weight sulfur-containing degradation products were formed which complex with copper.

The effectiveness of insoluble starch xanthate to remove heavy metals from water can be seen in Table VIII. Ten heavy metals were removed from separate metal solutions, in most cases to concentrations below present discharge limits. With a starch xanthate containing 8% sulfur and assuming a 1:1 mole ratio of monovalent metal ion to xanthate group, the binding capacity would be 1.1 mmoles metal per gram insoluble starch xanthate.

From our exploratory studies on the preparation of crosslinked starch xanthate, the following conditions gave the best results based on product quality and estimated cost to make. Starch is crosslinked at 40% solids, followed without isolation by xanthation at 25% solids for 1-4 hr, and the separated product is isolated by spray or flash drying. Effluents from the crosslinking of the starch

and from the xanthation contain considerable caustic. These effluents could be reused in further xanthations as previously described or they could be used to neutralize acidic wastes from other plant processes.

A preliminary cost-to-make estimate, based on laboratory studies, for dry insoluble starch xanthate is \$0.20–0.22 per pound. Costs are based on synthesis of an insoluble corn starch xanthate containing 8% S and isolation of the product by flash or spray drying. A plant producing 2.4 million lb per year is assumed, and estimated costs include charges for raw materials (March 1974 prices), utilities, labor and supervision, maintenance, depreciation, taxes and insurance, miscellaneous factory supplies and expenses, and general plant overhead.

### SUMMARY

Starch xanthates have been prepared which are insoluble in water. Conditions have been evaluated to give a method for making these products on a large scale. Insoluble starch xanthate has been shown to be effective in removing heavy metals from water to concentrations below established discharge limits.

The authors thank Bonita Heaton and Clara McGrew for running the chemical analysis; Art Eldridge for spray drying; and J. E. Boyle, The Hubinger Company, for crosslinked starch samples.

The mention 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.

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Received September 23, 1974