

# Starch Graft Polymers. I. Graft Co- and Terpolymers of Starch with 2-Hydroxy-3-methacryloyloxypropyltrimethylammonium Chloride and Acrylamide: Preparation and Evaluation as Silica Depressants\*

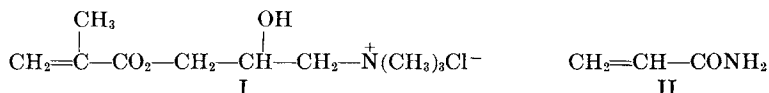
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## Synopsis

The title monomers have been grafted onto wheat starch by  $\gamma$ -radiation-induced polymerizations in water providing three graft polymers containing poly[2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride (I)] and two graft polymers containing poly[I and acrylamide (II)]. Characterization is discussed together with their utility as silica depressants in flotation-beneficiation of siliceous ores. Results are provided to illustrate that a starch graft copolymer containing 15% poly(I) graft and a graft terpolymer containing 30% poly(I, II) in the ratio 1:2 are effective as selective depressants for silica in flotation-beneficiation of Florida pebble phosphate ore using special flotation conditions.

## INTRODUCTION

Published research on starch graft polymers (SGP) to date has been devoted mostly to development of grafting procedures and product characterization, with much less attention given to investigation of the properties or industrial utility of the products. As part of a program designed to determine the technical and economical value of SGP in industrial applications, we have prepared and evaluated graft co- and terpolymers of starch and the vinyl monomers 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride (I) and acrylamide (II):



Described here is the preparation, characterization, and the laboratory evaluation of these products as silica depressants in flotation-beneficiation of Florida pebble phosphate ore.

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## EXPERIMENTAL

### Materials and Equipment

Unmodified wheat starch (Aytex P, General Mills Chemicals) and the vinyl monomers I (Shell Chemical Co.) and II (Matheson, Coleman, and Bell) were used in polymerization reactions without purification.

Irradiations were conducted in a Gammacell 220 cobalt-60 source (Atomic Energy of Canada) providing an irradiation field of 0.91 megarad/hr.

Flotation studies were conducted with washed sand (30–60 mesh; Walker Chemicals) and with flotation-grade phosphate ore (16–35 mesh) from the Nora Lynn Mine of International Minerals and Chemical Company, Bartow, Florida.

### Preparation of Starch Graft Polymers (SGP)

SGP were prepared by  $\gamma$ -radiation-induced polymerization of I and II on wheat starch suspended in water. In a typical reaction, 100 g of starch (9.8% moisture) was irradiated to 5.0 megarads at a dose rate of 0.91 megarad/hr, suspended in an aqueous solution of the vinyl monomers (475 ml water for reactions with I; 550 ml for reactions with I and II), and allowed to react for 2.0 hr at 25–30°C. To minimize interference by atmospheric oxygen, starch irradiations and grafting reactions were conducted in a nitrogen atmosphere, and monomer solutions were sparged with a slow stream of nitrogen for 30 min prior to addition of starch.

Products were recovered from reaction mixtures by decantation after dilution with 1 volume of isopropanol and were extracted successively with a 1:1 water-isopropanol mixture and isopropanol, filtered, and dried in vacuo at 40°C.

Products were characterized for nitrogen, chlorine, and moisture, and these values were used to calculate graft content and graft composition.

### Flotation Procedures

Screening studies of products as silica depressants were conducted as follows: A suspension of 30–60 mesh sand (washed but unfired) in water was conditioned (mixed) successively with depressant and collector (each for 4 min) and floated by subaeration with a stream of compressed air for 2 min. The overflow was collected, filtered to recover floated sand, dried, and weighed. Proportions used were 40 g sand, 360 ml tap water, 5.0 ml depressant (0.10% solution), and 2.0 ml of collector (Alamine 26 acetate; 1.0% aqueous solution).

Flotation studies with phosphate ore were conducted in a Denver laboratory flotation cell using 1.0-kg samples (dry weight) of deslimed, flotation-grade (16–35 mesh) ore preconditioned at 70% solids with flotation reagents in a drill-press conditioning cell. Flotation reagents—tall oil fatty acid and No. 5 fuel oil—were added as a 1:1 mixture after addition of

caustic. Depressants were added as 0.10% dispersions prior to addition of flotation reagents after initial studies indicated products were less effective if added with or after flotation reagents. Overflow and tailing fractions were recovered by filtration, dried, and weighed. Portions of each were analyzed for phosphorous pentoxide and hydrochloric acid insolubles, and results were reported as BPL (bone phosphate of lime; tricalcium phosphate) and acid insolubles content.

## RESULTS AND DISCUSSION

Study of products in this application was prompted by the observation that cationic (but not anionic and nonionic) SGP flocculate colloidal silica and conceivably could depress silica in flotation-beneficiation of silica-containing mineral ores.

### Preparation and Characterization of SGP

Grafting reactions were conducted by  $\gamma$ -radiation-induced grafting reactions patterned after those described by Reyes.<sup>1</sup> The SGP shown in Table I retained the discrete granular structure of starch and could be isolated from reaction mixtures by filtration. Rate of filtration decreased with increased graft (e.g., SGP-3 and 5); consequently, reaction mixtures were diluted with 1 volume of isopropanol to provide a practical filtration rate. Unreacted monomer and ungrafted homopolymers are soluble in aqueous isopropanol (1:1) as shown by separate studies with poly(I) and poly(I, II) prepared by radiation-induced solution polymerization and hence are removed from graft polymer products during filtration and washing; their relative proportions in the filtrates were not determined.

TABLE I  
Radiation-Induced Synthesis<sup>a</sup> of Starch Graft Polymers (SGP)  
Used in Flotation Studies

Reaction no.	Vinyl monomer, g		Product yield, g	Nitrogen content, %	Monomer in product <sup>d</sup>	
	I <sup>b</sup>	II <sup>c</sup>			I	II
SGP-1	9.10	...	102	0.147	2.5	...
SGP-2	18.20	...	104	0.41	6.9	...
SGP-3	36.4	...	112	0.89	14.9	...
SGP-4	1.82	5.0	101	0.31	... <sup>e</sup>	... <sup>e</sup>
SGP-5	18.2	50.0	125	4.55	10.8	19.8

<sup>a</sup> Reactions were conducted by addition of starch (100 g, 9.8% moisture), preirradiated in a cobalt 60 source to 5.0 megarads at a dose rate of 0.91 megarad/hr, to solutions of the monomer(s) in water (475 ml for reactions 1-3; 550 ml for reactions 4 and 5). Reaction time and temperature were 2.0 hr and 25-30°C, respectively.

<sup>b</sup> I is 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride.

<sup>c</sup> II is acrylamide.

<sup>d</sup> I content was calculated from chloride analyses; II content was determined from nitrogen content corrected for I nitrogen, for starch nitrogen, and for moisture.

<sup>e</sup> Nitrogen and chlorine values too low for accurate estimation.

Poly(I) content of terpolymers prepared with compounds I and II was calculated from chlorine content. Poly(II) content of terpolymers was calculated from nitrogen content corrected for nitrogen content contributed by poly(I).

Chemical bonding of polymeric chains to the starch backbone was not investigated in depth. However, evidence supporting chemical grafting, established by Reyes in analogous reactions,<sup>1</sup> was provided by extraction studies with one product (reaction SGP-3, Table I). This product, which contained 14.9% poly(I), was extracted three times with water at 40°C. Water extracts were combined, diluted with isopropanol (which did not cause precipitation), and freeze-dried yielding a solid residue (3A) corresponding to 10.2% of the initial product. Elemental analyses of 3A and the water-insoluble residue (3B) showed them to contain 3.6% and 0.50% nitrogen, respectively, which corresponds to graft contents of 61% and 8.5%. In view of the reported water extractability of poly(I) from mixtures with starch,<sup>2</sup> 3B is not a mixture of ungrafted starch and poly(I). On the other hand, presence of ungrafted starch in 3A is unlikely in view of the product's solubility in aqueous isopropanol. On the basis of these considerations, it appears reasonable to conclude that 3B is a graft copolymer and 3A is a highly grafted copolymer or a mixture of graft copolymer and poly(I).

### Evaluation as Silica Depressants

To estimate the effectiveness of cationic SGP as silica depressants, a series of flotation runs were made with sand and a fatty amine collector (a good flotation aid for sand). Results, tabulated in Table II, show that SGP-2 and SGP-5, containing 6.9% poly(I) and 30.6% poly(I, II), respectively, are the most effective of the SGP evaluated. Both products provided essentially complete depression of sand flotation in the trials. Products are, in

TABLE II  
Depressant Action of SGP in Flotation<sup>a</sup> of Sand with a Cationic Collector<sup>b</sup>

Additive	Description	Additive level, lb/ton	Amount floated, g	Sand depressed, %
SGP-1	see Table I	0.25	4.04	89.9
SGP-2	see Table I	0.25	0.18	99.5
SGP-4	see Table I	0.25	12.7	68.1
SGP-5	see Table I	0.25	0.50	98.8
Aytex P <sup>c</sup>	wheat starch	0.25	28.7	27.7
Control 1	cationic starch	0.25	1.03	97.4
Control 2	cationic PAA	0.25	0.49	98.8
—	blank	—	39.7	—

<sup>a</sup> Flotations were conducted in a 400-ml beaker using 40 g sand (30–60 mesh) in 360 ml water, 5 mg depressant as a 0.10% solution, and 20 mg collector in a 1.0% solution.

<sup>b</sup> Alamine 26 acetate (General Mills Chemicals, Inc.).

<sup>c</sup> General Mills Chemicals, Inc.

addition, vastly superior to unmodified starch in this respect and are slightly superior to a conventional cationic starch and a cationic polyacrylamide (PAA) included in the study for comparison purposes.

These results established that cationic SGP have silica depressant activity. To determine their utility as silica depressants in flotation processes in which nonsiliceous matter is floated from siliceous matter—processes in which an effective silica depressant would have utility—SGP 2, 3-, and -5 were studied in flotation-beneficiation of Florida pebble phosphate ore. This ore is a mixture of sand and phosphate particles of similar size distributions. Inseparable by mechanical means, the mixture can be separated by flotation and is presently subjected to a two-stage flotation<sup>3</sup> yielding a product containing 70–75% BPL (bone phosphate of lime or tricalcium phosphate) and 4–5% acid insolubles (sand). In the first stage, flotation with an anionic collector floats the bulk of the phosphate together with some sand. After washing, the primary float is refloatated with a cationic collector which floats the sand. Purification in this manner gives a flotation concentrate containing about 72% BPL and 4–5% acid insolubles. While separation efficiency and phosphate recovery provided by this process is generally satisfactory, depression of silica in the primary flotation stage obviously would eliminate the need for a second flotation, thereby simplifying the process and making it more economical.

Data for evaluation of SGP as silica depressants in flotation beneficiation of phosphate ore are given in Tables III to VIII. Studies were conducted with flotation feedstock and flotation reagents obtained from International Minerals and Chemical Company, Bartow, Florida. The ore used contained 35.7% BPL and 56.5% acid insolubles and was reported to give a commercial product, in 50–55% yield, containing 72–74% BPL and 4–5% acid insolubles.

TABLE III  
Flotation Studies with Florida Pebble Phosphate Ore<sup>a</sup>—  
Effect of Order on Addition of Reagents on SGP Depressant Activity

Run no.	Flotation conditions <sup>b</sup>	Flotation product	Yield, %	Analyses, %		BPL recovery, %
				BPL <sup>c</sup>	Insols <sup>d</sup>	
1	blank (no SGP)	float	51.2	71.5	11.8	92.2
		tails	48.8	6.3	90.5	—
2	SGP <sup>e</sup> added with flotation reagents	float	50.0	72.2	10.5	89.9
		tails	50.0	8.1	88.2	—
3	SGP <sup>e</sup> added before flotation reagents	float	41.4	75.7	7.2	78.1
		tails	58.6	15.1	80.5	—

<sup>a</sup> Composition of ore (16–36 mesh): 35.7% BPL, 56.5% acid insolubles.

<sup>b</sup> Flotations were conducted at pH 8.9 in a Denver flotation cell using 1.0 kg (dry basis) of ore conditioned with 1.14 lb/ton each of tall oil fatty acid and No. 5 fuel oil.

<sup>c</sup> Bone phosphate of lime (tricalcium phosphate).

<sup>d</sup> Hydrochloric acid insolubles (silica).

<sup>e</sup> SGP-5 in Table I.

TABLE IV  
Flotation Studies with Florida Pebble Phosphate Ore<sup>a</sup>—Variation of Collector Level

Run no.	Additive level, lb/ton		Flotation product	Yield, %	Analyses, %		BPL recovery, %
	SGP	Collector <sup>b</sup>			BPL	Insols	
4	—	0.91	float	52.9	69.6	12.6	93.6
			tails	47.1	5.3	91.5	—
5	—	1.14	float	54.1	68.8	14.3	94.1
			tails	45.9	5.1	91.7	—
6	—	1.37	float	58.1	64.6	18.4	95.6
			tails	41.9	4.0	93.0	—
7	—	1.82	float	60.6	63.6	20.5	97.0
			tails	39.4	3.0	94.8	—

<sup>a</sup> Composition of ore and flotation conditions are given in footnotes to Table III.

<sup>b</sup> Tall-oil fatty acid; added as a 1:1 mixture with No. 5 fuel oil.

TABLE V  
Flotation Studies with Florida Pebble Phosphate Ore<sup>a</sup>—  
Variation of Starch Graft Polymer<sup>b</sup> Addition Level

Run no.	Additive level, lb/ton		Flotation product	Yield, %	Analyses, %		BPL recovery, %
	SGP <sup>b</sup>	Collector <sup>c</sup>			BPL	Insols	
8	0.025	1.14	float	36.0	73.6	9.5	67.7
			tails	64.0	19.7	63.0	—
9	0.050	1.14	float	38.5	74.4	8.8	73.0
			tails	61.5	17.2	66.4	—
10	0.100	1.14	float	43.4	72.8	10.1	79.4
			tails	56.6	14.5	60.0	—
11	0.200	1.14	float	53.0	70.4	12.9	94.3
			tails	47.0	4.8	90.2	—
5	—	1.14	float	54.1	68.8	14.3	94.1
			tails	45.9	5.1	91.7	—

<sup>a</sup> Composition of ore and flotation conditions are given in footnotes to Table III.

<sup>b</sup> SGP from reaction 5, Table I.

<sup>c</sup> Tall-oil fatty acid; added as a 1:1 mixture with No. 5 fuel oil.

Initial studies (Table III) established that SGP-5 depressed silica during flotation if added to the ore before the flotation reagents. Studies also revealed that the SGP partially depressed phosphate under the conditions used.

To evaluate the effectiveness of SGP products as silica depressants in this application under various conditions, a series of evaluations were conducted similar to control runs (Table IV) but with SGP-5 at varying levels of addition and holding collector level constant (Table V), and at varying collector levels and holding SGP-5 level constant (Table VI). Results relative to control runs made at varying collector levels without added SGP (Table IV) determined the graft polymer level, providing maximum silica depression is

0.05 lb/ton. Relative effectiveness of the SGP and reference standards evaluated as silica depressants is shown in Table VII. Results show that the most effective SGP products is a graft copolymer of starch and com-

TABLE VI  
Flotation Studies with Florida Pebble Phosphate Ore<sup>a</sup>—  
Effect of Collector Level on the Depressant Action of SGP<sup>b</sup>

Run no.	Additive level, lb/ton		Flotation product	Yield, %	Analyses, %		BPL recovery, %
	SGP <sup>b</sup>	Collector <sup>c</sup>			BPL	Insols	
5	—	1.14	float	54.1	68.8	14.3	94.1
			tails	45.9	5.1	91.7	—
12	0.05	0.91	float	38.9	74.6	8.0	74.3
			tails	61.1	16.4	67.2	—
13	0.05	1.14	float	38.5	74.4	8.8	73.0
			tails	61.5	17.2	66.4	—
14	0.05	1.37	float	41.1	72.2	10.9	75.6
			tails	58.9	16.3	67.4	—
15	0.05	1.82	float	44.2	69.7	13.1	77.9
			tails	55.8	15.7	68.5	—

<sup>a</sup> See footnotes to Table III for composition of ore and for flotation conditions.

<sup>b</sup> SGP-5, Table I, was used in these studies.

<sup>c</sup> Tall-oil fatty acid; added as a 1:1 mixture with No. 5 fuel oil.

TABLE VII  
Evaluation of SGP as Silica Depressants in Flotation-  
Beneficiation of Florida Pebble Phosphate Ore<sup>a</sup>

Run no.	Description	Additive used <sup>b</sup> Amount, lb/ton	Flotation product	Yield, %	Analyses		BPL recovery, %
					BPL	Insols	
16	SGP-2 <sup>c</sup>	0.05	float	45.5	72.6	10.0	84.6
			tails	54.5	11.0	84.2	—
17	SGP-3 <sup>c</sup>	0.05	float	37.6	75.9	7.0	73.2
			tails	62.4	16.7	77.0	—
9	SGP-5 <sup>c</sup>	0.05	float	38.5	74.4	8.8	73.0
			tails	61.5	17.0	66.4	—
18	Starch <sup>d</sup>	0.10	float	54.1	65.0	15.9	96.8
			tails	45.9	2.7	95.3	—
19	Control-2	0.10	float	53.3	66.0	18.1	90.5
			tails	46.7	8.0	87.3	—
20	Control-3 <sup>e</sup>	0.25	float	50.0	67.0	11.4	91.5
			tails	50.0	6.2	90.1	—

<sup>a</sup> See footnotes to Table III for description of the ore and of flotation conditions.

<sup>b</sup> Tall-oil fatty acid mixed with No. 5 fuel oil (1:1) was used as collector in flotations at an addition level of 1.14 lb/ton each.

<sup>c</sup> See Table I for composition of the products.

<sup>d</sup> Wheat starch (General Mills Aytex P).

<sup>e</sup> Cationic starch (different from control-1).

TABLE VIII  
Flotation Studies with Florida Pebble Phosphate Ore<sup>a</sup>—  
Effect of Reflotation of Primary Float Concentrate<sup>b</sup>

Run no.	Additive level, lb/ton		Flotation product	Yield, %	Analyses, %		BPL recovery, %
	SGP <sup>c</sup>	Collector <sup>d</sup>			BPL	Insols	
20	0.05	0.91	float	29.1	78.7	4.5	57.1
			no. 1 tails	54.3	13.4	81.1	—
			no. 2 tails	16.6	59.8	26.2	—
21	0.05	1.14	float	30.4	78.8	4.1	69.2
			no. 1 tails	53.0	8.9	71.6	—
			no. 2 tails	17.0	62.3	21.6	—
22	(Blank)	1.14	float	48.8	72.1	7.1	94.6
			no. 1 tails	41.3	2.5	95.9	—
			no. 2 tails	10.9	5.6	89.3	—

<sup>a</sup> Composition of the ore and flotation conditions are given in footnotes to Table III.

<sup>b</sup> The primary float concentrate was returned to the flotation cell after removal of the first tails (no. 1 tails), made up to volume with water and refloatated without additional reagents to give a float and a second tails (no. 2 tails).

<sup>c</sup> SGP-5, Table I.

<sup>d</sup> Tall-oil fatty acid mixed 1:1 with No. 5 fuel oil.

pound I containing 14.9% graft (SGP-3, Table I). In contrast, a cationic starch and a cationic polyacrylamide showed no effect as silica depressants.

To determine if flotation of phosphate traps depressed silica in the over flow during flotation, the float concentrate in two runs was returned to the flotation cell and refloatated without additional reagents (Table VIII). Results show that this procedural modification significantly improves separation of silica from the float concentrate, yielding a marketable-grade product directly (i.e., BPL above 75%; acid insolubles below 5.0%). Recovery of BPL values is low, however, which makes the use of SGP products as silica depressants uneconomical unless phosphate-rich tailing fractions (no. 2 tails) are recycled to recover phosphate content.

In summary, preliminary studies of cationic SGP as silica depressants in flotation-beneficiation of Florida pebble phosphate ore have established that the graft polymers depress silica during anionic flotation of phosphate ore. The magnitude of the depressant action is not sufficient to eliminate the need for the customary secondary cationic flotation to lower the excess silica content of the products. However, simple refloatation of the primary float without additional reagents decreases silica content sufficiently to provide a marketable product. Reflotation of the primary float in this manner decreases yield and BPL recovery, rendering its adoption uneconomical unless secondary float tailings are recycled. With this modification, BPL losses can be minimized, flotation reagent costs can be lowered, and the overall cost of flotation-beneficiation of phosphate can be decreased.



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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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