Starch-Derived Polyelectrolytes as Builders in Heavy Duty Detergent Formulations

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Abstract

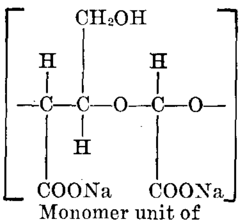
A study was made of some carboxylated starches as builders in detergent formulations that contained linear alkylbenzene sulfonate. Two types of standard soiled cotton were used with water at 300 ppm hardness. Dicarboxyl starches and carboxymethyl starches having approximately two carboxyl groups per monomer unit were as effective as sodium tripolyphosphate on an equal weight basis in the detergent formulation. In a five-day biochemical oxygen demand test these products showed low biodegradability.

Introduction

The overall program of the Federal Water Quality Administration stresses the reduction of phosphates in sewage effluents because of their presumed contribution to accelerated eutrophication (1). A source of phosphate contamination in lakes and streams is the sodium tripolyphosphate (STPP) builder used in household laundry detergents (2). One approach to the solution of this problem is the development of biodegradable organic builders to replace STPP (3). In 1943, Höppler (4) showed the efficacy of using carboxymethyl starch with detergents for soil removal, and later, the similar application of other ethers (5) and starch esters (6) was described. Dicarboxyl starches (7) have also been suggested for use with detergents to improve washing performance. More recently, Eldib (8,9) investigated various starch polyelectrolytes and stated that certain carboxylated starch products were highly effective detergent builders.

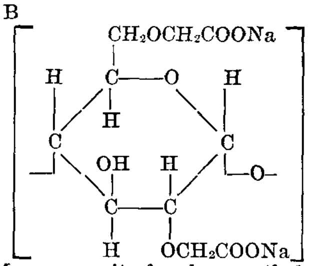
In a screening program on organic builders as complete replacements for STPP, we evaluated a number of starch derivatives in a standard heavy duty formulation containing linear alkylbenzene sulfonate (LAS). Detergency was determined with two different types of soiled cotton in hard water. Many polymer products investigated contained a plurality of carboxyl and hydroxyl groups because these, in appropriate combination, are known to sequester alkaline earth metal ions in hard water (10). Those with the unit structures shown in A and B were the most effective builders studied.

A



Monomer unit of dicarboxyl starch

B



Monomer unit of carboxymethyl starch

Experimental Procedures

Materials

The dicarboxyl starches were prepared by sodium chlorite oxidation of various dialdehyde starches (7,11). Dialdehyde starch of more than 90% carbonyl content (Sumstar 190) was supplied by Miles Laboratories, Inc., Elkhart, Ind. The other dialdehyde starches were synthesized by sodium periodate oxidation of unmodified (12), acid-modified and epichlorohydrin crosslinked corn starches (13). Unmodified corn starch was Globe Starch No. 3001 and acid-modified starch was Eagle Brand No. 5082, both products of CPC International, Argo, Ill.

Carboxymethylated products were made by reaction of sodium chloroacetate with the starches according to the method of Sloan et al. (14).

Standard detergent was Conoco SA-697, a 97% active linear alkylbenzene sulfonic acid manufactured by Continental Oil Company, New York. Standard soiled cotton was purchased from Foster D. Snell, Inc., subsidiary of Booz-Allen Applied Research, Inc., Florham Park, N.J., and ACH Fiber Service, Inc., Boston, Mass.

Detergency

Soil removal was first conducted with a standard heavy duty detergent containing 15% Conoco SA-697 (neutralized with sodium hydroxide), 50% STPP, 24% sodium sulfate, 10% sodium metasilicate and 1% carboxymethylcellulose (CMC) to determine the detergency of the STPP formulation as a basis for comparison with the starch-derived builders. In the experimental formulas the STPP was replaced with an equal weight of the various polyelectrolytes unless otherwise noted. Reflectance was measured after washing six swatches of 4 × 4 in. standard soiled cotton in 1 liter of detergent solution in a Terg-O-Tometer for 20 min at 60 C and 105 cycles/min. Two different kinds of standard soiled cotton [Foster D. Snell (FDS) and ACH Fiber Service No. 115A (ACH)] were used. All tests were conducted in water of 300 ppm of hardness.

Reflectance measurements were made with a Martin-Sweets automatic color brightness tester, and relative detergency values were compared as ΔR (Table I). By analysis of variance the least significant differences in ΔR at 95% probability were determined.

From Table I it is apparent that both dicarboxyl and carboxymethyl starches require high percentages of carboxyl units before they perform as efficiently as STPP. Based on carboxyl content, the carboxy-

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TABLE I

Detergency of Solutions[a] *Containing Starch-Derived Builders*

Builders[b]	Substitution	Standard soiled cotton[c] FDS: ΔR starch prod.	FDS: (ΔR, starch prod. / ΔR, STPP) × 100	ACH: ΔR starch prod.	ACH: (ΔR, starch prod. / ΔR, STPP) × 100
Dicarboxyl derivative of:					
Pearl corn starch	60[d]	8.4[4 e]	48	24.8[2]	83
	75	....	....	28.1[1]	90
	90			28.6[2]	95
	90			24.3[2]	81[f]
Acid modified	94			28.9[1]	93
Crosslinked					
10 AGU/CL[g]	83			30.2[2]	101
700 AGU/CL	98	12.6[4]	77	31.6[2]	105
2500 AGU/CL	90	12.2[3]	92	29.6[1]	95
Amylose fraction	87	....	....	25.3[1]	81
Amylopectin fraction	86	16.6[4]	101	31.5[2]	105
Carboxymethyl derivative of:					
Pearl corn starch	0.6[h]	....	....	19.6[1]	63
	1.0	5.1[3]	38	25.7[1]	83
	2.2	14.2[4]	87	29.5[1]	95
	2.2	9.5[4]	58	25.1[2]	84[f]
Acid modified	1.0	....	....	24.4[2]	81
	2.0	11.2[4]	68	27.1[2]	90
Crosslinked					
700 AGU/CL	2.2	12.5[4]	76	26.4[2]	88
High amylose 70%	0.83	8.9[4]	54	22.7[2]	76
	2.1	11.9[4]	73	25.4[2]	85
Amylopectin fraction	1.3	....	....	29.9[2]	100
	1.9	12.0[4]	73	32.1[2]	107
Significance level[i]		3.2		3.2	

[a] Made up of 0.023% active detergent and 0.075% builder (exclusive of sodium sulfate, sodium metasilicate and carboxymethylcellulose) in hard water (300 ppm).
[b] Builder as neutral sodium salt was 50 wt % of the detergent formulation.
[c] FDS, Foster D. Snell; ACH, ACH Fiber Service No. 115A.
[d] Per cent carbonyl content of the theoretical for dicarboxyl starches.
[e] 1–4: Different lots of standard soiled cotton.
[f] Builder is 25 wt % of the detergent formulation, the remainder being substituted by sodium sulfate.
[g] Anhydroglucose units per crosslink.
[h] Degree of substitution (D.S.) of carboxymethyl starches.
[i] Differences in ΔR of the values listed are significant with 95% probability.

methyl unit may be slightly more effective in soil removal. Lowering the molecular weight of these products by acid hydrolysis of starch before substitution of carboxyl groups did not appreciably change their builder properties. Carboxylated corn starches (13,15) and the carboxylated amylose and amylopectin fractions of corn starch also performed well as builders when the carboxyl content was high. Utilizing, however, only 25 wt % of dicarboxyl corn starch of 90% oxidation and of carboxymethyl corn starch of degree of substitution (DS) 2.2 in the standard detergent formulation produced inferior detergency.

Detergency varied with the soiled cotton used. Values were higher with the ACH soiled cotton than with FDS cloth. A complete study with the latter was impossible because the soiled cotton became unavailable soon ofter the project began.

Biological Degradation of Starch-Derived Builders

In addition to being effective for soil removal, organic builders for heavy duty detergent formulations must be highly biodegradable in surface waters to avoid replacement of inorganic by stable organic pollutants. The five-day biochemical oxygen demand (BOD) test is only an indication of susceptibility of products to biodegradation but is a first step in predicting their behavior in a water-treatment plant and in surface waters. Unmodified corn starch is nearly 70% degraded in this fashion in five days (16), as shown in Table II, and is readily removed from waste water in an activated sludge system (17). However, introduction of carboxyl groups into starch as in dicarboxyl starch completely changes the anhydroglucose monomer structure of the polysaccharide so that similar biodegradability cannot be expected. Data show that it is more difficult to biodegrade the dicarboxyl starches than starch itself. In carboxymethylated starches the ring anhydroglucose monomer units of starch remain intact while the hydroxyl groups are converted to ethers by attachment of carboxymethyl groups. As is known for CMC (16), such substitution greatly hinders enzyme action and results in low biodegradability. Oxygen utilized by microorganisms metabolizing dicarboxyl starch was 30% of the theoretical in five days, whereas that for the carboxymethyl starch of DS 2.2 was only 8.8%. Disruption of the granule structure of the starch products by cooking in water at 100 C for a few minutes before testing greatly improved the five-day BOD.

Results and Discussion

Soil removal studies with an LAS detergent formulation containing 50 wt % of various starch derivatives showed that dicarboxyl starches and carboxymethyl starches having approximately two carboxyl groups per monomer unit were as effective as STPP on an equal weight basis. Presumably, the better builder properties of these starch derivatives are partly due to improved sequestration of calcium ions with the increase in the number of chelate rings in their structures. Maximum substitution in carboxy-

TABLE II

Biochemical Oxygen Demand (BOD) of Carboxylated Starches

Builder[a]	BOD, five-day mgO_2/mg	% of theory[b]
Dicarboxyl starch (90% dicarboxyl)	0.24[c]	30
	0.135	17
Carboxymethyl starch (DS 2.2)	0.088[c]	8.8
	0.024	2.4
Corn starch (control)	0.82[c]	69

[a] Neutral sodium salts: concentration 125 ppm.
[b] For complete degradation.
[c] Cooked at 100 C before test.

methyl starch is attained at a DS of 3, but this level of etherification is difficult to achieve economically and was not investigated. In fact all the starch derivatives found to have promising builder action are considerably more costly to produce than STPP and their consideration as replacements for this compound must be questioned at this time. Furthermore, these potential builders are not highly biodegradable in a five-day BOD test.

This study of a limited number of starch derivatives as builders in LAS detergent formulations has indicated some types of structures effective for soil removal and corroborates the results of previous investigators.

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