

## **Base-Hydrolyzed Starch-Polyacrylonitrile (S-PAN) Graft Copolymer. S-PAN-1:1, PAN M.W. 794,000\***

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### **Synopsis**

Starch-polyacrylonitrile (S-PAN) graft copolymer consisting of one part starch and one part polyacrylonitrile (M.W. 794,000) was hydrolyzed with aqueous KOH at 80 and 100°C to polyelectrolytes containing carboxyl and amide functionality but void of infrared-detectable amounts of nitrile. Viscosities of potassium salts of the polyelectrolytes in water were pH dependent with peak viscosities at 8.5. These dispersions were characterized by unusually high viscosities, 15,000 to 26,500 cp at 1% concentration, and by the ability to retain significant viscosities, 300 to 950 cp, upon dilution to 0.03% concentrations. A 1% dispersion of hydrolyzed S-PAN had a viscosity of 5,000 cp in the presence of 8% KCl; however, the depressing effect of added salts on viscosity of aqueous dispersions of hydrolyzed S-PAN increases as the valence of the cation increases.

### **INTRODUCTION**

The preparation of starch graft copolymers from various vinyl monomers and by different initiation systems has been described.<sup>1-8</sup> Most starch-graft copolymers prepared by free radical processes, except those made from acrylamide, acrylic acid, and methacrylic acid, are insoluble in water and common organic solvents. To our knowledge, however, no detailed study has been made on the solution properties of starch-graft copolymers. Base hydrolysis of starch-polyacrylonitrile (S-PAN) gives a water-soluble polymer. Since aqueous dispersions of starch and simple starch derivatives are important in many applications, it was of interest to study the hydrolysis of S-PAN and the solution properties of the resulting products.

Our objectives were the conversion of refined and well-characterized S-PAN graft copolymers into water-soluble polymers and the determination of their properties, particularly solution viscosities. Toward these ends we investigated the alkaline hydrolysis of purified S-PAN consisting of one part by weight of polyacrylonitrile (PAN) (794,000 M.W.) and one part by weight of starch (S). This copolymer (S-PAN-1:1) was prepared<sup>8</sup> by grafting acrylonitrile onto a gelatinized wheat starch previously treated

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with ceric ammonium nitrate initiator. Reported here are conditions for preparation and isolation of hydrolyzed (H) S-PAN products and data on the effects of pH, salts, and concentration of HS-PAN on dispersion viscosities.

## EXPERIMENTAL

### Preparation of S-PAN-1:1

Quantities of materials were proportional to those used by Fanta et al.<sup>8</sup> Weights of all starting materials and products are given on a moisture-free basis. Wheat starch (42.37 g) was gelatinized in 400 ml of water at 85°C under nitrogen with stirring for 1 hr. The mixture was cooled to 25°C and 14.6 ml of 0.1 *M* ceric ammonium nitrate reagent made up in 1 *N* HNO<sub>3</sub> was added. After a 20-min initiation period, 61.6 g of distilled acrylonitrile was added to the reaction mixture which was kept under nitrogen. Since the polymerization was exothermic, the temperature was maintained at 30 to 33°C by cooling. After 3 hr reaction, the product was recovered by filtration and washed with water until free of acid and unreacted acrylonitrile. The weight of the air-dried solid was 73.5 g.

A water-soluble fraction removed from the crude product by extraction at 90°C for 2½ hr with 1 l of water amounted to 5.03 g. The insoluble fraction was air-dried and amounted to 64.7 g. Extraction of this material with 1500 ml of dimethylformamide at room temperature removed 2.5 g of solubles. Insoluble material, first washed with ethyl alcohol and then with water, afforded 56.5 g of S-PAN after being air-dried.

### Alkaline Hydrolysis of S-PAN-1:1

Hydrolysis of S-PAN-1:1 at 80 and 100°C in the presence of varying amounts of aqueous KOH for 2 and 3 hr gave mixtures from which HS-PAN-1:1 products in free-acid form were isolated. S-PAN-1:1 (7.96 g) was heated in a 500-ml glass-stoppered Erlenmeyer flask containing 314 ml of approximately 4, 8, or 16% KOH solution. The flask was cooled in ice and concentrated HCl added slowly with vigorous stirring until, at pH 3, a white solid was precipitated and recovered by centrifugation. The solid was slurried in water and recentrifuged. This process was repeated until the wash water was almost neutral. The product was dried with absolute ethanol and then air-equilibrated.

### Viscosity Measurements

Samples of approximately 0.25 g were weighed in glass vials (30 mm × 75 mm) and 0.100 *N* KOH was added to achieve dispersion and regulate pH. Finally, deionized water was added to make 1% dispersions. They were stirred and then kept overnight before viscosity measurements were made at 25°C with a Brookfield Synco-lectric viscometer, LVT. Dispersions of lower concentrations were made by appropriate dilutions of 1% dispersions.

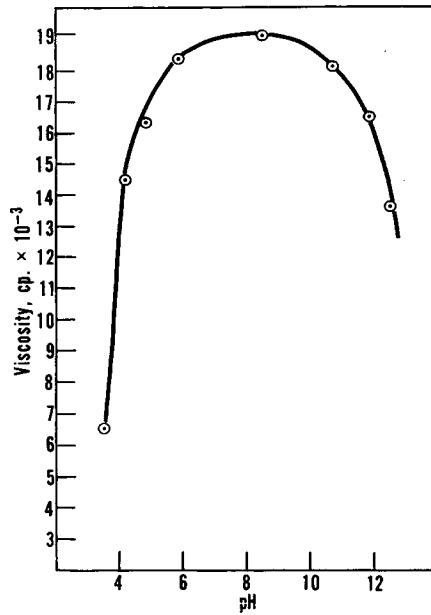


Fig. 1. Viscosity vs. pH of 1% dispersion of hydrolyzed starch-polyacrylonitrile graft copolymer, HS-PAN-1:1 (Prep. 3), 25°C, 30 rpm, and No. 4 spindle.

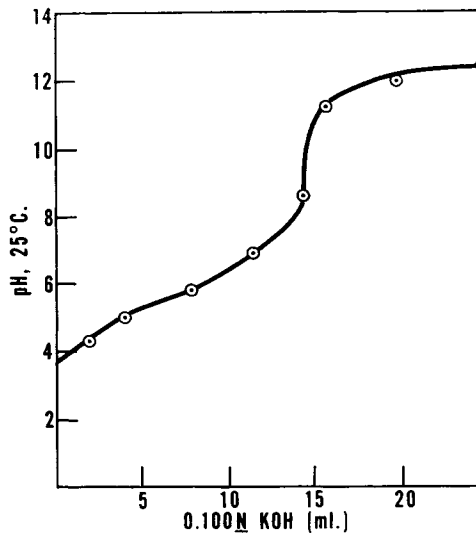


Fig. 2. Potentiometric titration curve for Prep, 3; sample weight 0.2487 g.

### Titration of HS-PAN-1:1

Titration data on each HS-PAN-1:1 product were obtained from a series of 1% dispersions made for studying the effect of pH on viscosity (Fig. 1). Each dispersion had the same weight of HS-PAN-1:1 but a different volume

of 0.100 *N* KOH. The pH of each dispersion was determined, and from a plot of pH vs. ml KOH (Fig. 2) the percentage of carboxyl in the product was calculated. The end point of titration for each was pH 8.5.

### Molecular Weight of PAN Graft

Purified S-PAN-1:1 (4.67 g) was hydrolyzed in 450 ml of 1 *N* HCl for 2 hr at 95°C to yield 2.3 g of PAN. The intrinsic viscosity in dimethylformamide at 25°C was determined and the number-average molecular weight of PAN calculated from the Mark-Houwink equation using Onyon's constants.<sup>9</sup>

### Hydrolysis of PAN

Six grams of PAN was hydrolyzed with 300 ml of 8.65% KOH at 100°C for 2 hr. The mixture was cooled and concentrated HCl added with stirring. Hydrolyzed PAN, which precipitated at pH 3, was washed free of HCl, dried with absolute ethanol, and then equilibrated with air. The product (5.7 g) contained 6.87% N and 36.5% carboxyl. The theoretical carboxyl content for complete hydrolysis is 62.5%.

### Results and Discussion

The weight ratio of starch to PAN in the purified S-PAN-1:1, based on a carbon analysis of 56.03%, is 1:1; however, the nitrogen (Kjeldahl) analysis of 14.2% suggests that about 4% more PAN is present. A frequency of grafting value, i.e., anhydroglucose units per PAN chain, of 4623 was calculated from the S: PAN ratio and the number-average M.W. of PAN which is 794,000. These results are in good agreement with those reported by Fanta et al.<sup>8</sup>

### Hydrolysis of S-PAN-1:1

Insolubility at pH 3 of HS-PAN-1:1 products makes their isolation easy and may provide the key to a practical process for their recovery. In general, the precipitated products could be washed to remove KCl and excess HCl without serious swelling. Prep. 3 (Table I) was an exception. Upon continued washing, this material swelled and use of absolute ethanol was necessary to precipitate it.

Development of deep red color and its gradual disappearance during hydrolysis of S-PAN-1:1 is caused by the formation of naphthyridine ring structures<sup>10-12</sup> from PAN, which are subsequently saponified.<sup>13</sup> Although PAN coloration in the presence of alkali and investigation of functional groups present in partially saponified PAN<sup>13</sup> have been the subject of recent work, our current interest is in the properties of HS-PAN-1:1 products. The infrared spectrum of Prep. 3 (Fig. 3), which is typical for the HS-PAN's, shows no nitrile band but two strong carbonyl bands at 5.8 and 6.0  $\mu$ , which are due to nonionized carboxyl and amide, respectively. In the spectrum of a film made from a dispersion of Prep. 3 at pH 7.5, the

TABLE I  
Hydrolysis of Starch-Polyacrylonitrile (S-PAN)-1:1<sup>a</sup>

Prep.	KOH, g	Reaction conditions				Product, g	Yield, wt %	Analyses, %			Carboxyl, <sup>c</sup> wt %	
		Temp., °C	Time, hr	KCl, g	KOH: PAN (wt)			C	H	N <sup>b</sup>		Ash
1	13.6	80	3	0	2.7	8.8	88	48.3	6.57	6.06	0.4	21.1
2	27.2	80	2	0	5.4	8.5	85	48.2	6.65	5.90	0.18	23.0
3	27.2	100	2	0	5.4	8.15	81.5	48.82	6.75	4.40	0.51	26.6
4	54.4	100	2	0	10.8	8.65	86.5	48.74	6.34	4.81	1.30	22.2
5	27.2	100	2	10	5.4	8.0	80.0	48.8	6.76	4.40	0.50	23.0

<sup>a</sup> In each reaction were used 10 g S-PAN-1:1 and 314 ml of KOH solution.

<sup>b</sup> Kjeldahl nitrogen.

<sup>c</sup> Percentage of carboxyl for a theoretically complete hydrolysis is 36.2.

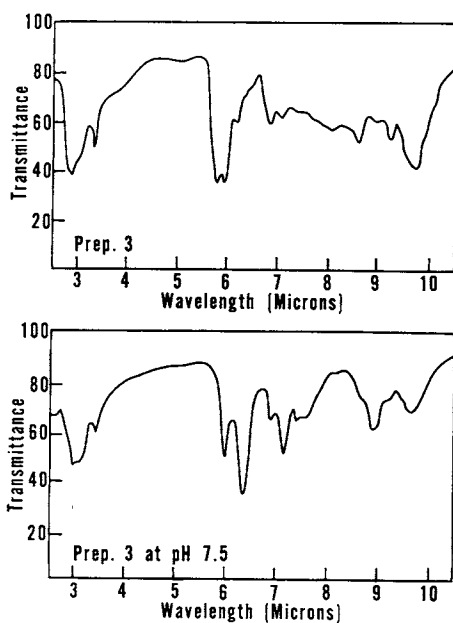


Fig. 3. Spectra of HS-PAN-1:1 in the presence and absence of KOH.

5.8  $\mu$  band is missing and a stronger band due to ionized carboxyl is present at 6.35  $\mu$ .

Hydrolysis of S-PAN-1:1 at 80 and 100°C employing KOH:PAN weight ratios from 2.7 to 10.8 (Table I) failed to yield nitrogen-free products containing the theoretical percentage of carboxyl; i.e., 36.2% corresponding to the complete conversion of nitrile to carboxyl. Although infrared spectra indicate that much of the nitrogen is present as amide, further hydrolysis of Prep. 4 under the same conditions used initially only lowered the nitrogen from 4.81 to 4.65% and increased the carboxyl from 22.2 to 23.1%. Also, hydrolysis in the presence of KCl (Prep. 5) failed to give significantly different results. Concentration of base used to make Prep. 4 was twice that used in Prep. 3; however, the former preparation had more nitrogen and less carboxyl. Failure to achieve complete conversion of the nitrile groups in S-PAN to carboxyl groups was not unexpected because Smets<sup>14</sup> and Moens and Smets<sup>15</sup> encountered the same difficulty in the base hydrolysis of polyacrylamide. They attributed this to the neighboring group effect of formed carboxyl groups which exert an increasing electrostatic repulsion toward hydroxyl ions as hydrolysis progresses. In addition, Nagase<sup>16</sup> suggests that the observed decrease in reaction rate during hydrolysis of polyacrylamide is due to increasing viscosity which retards movement of the polymer molecules and diffusion of reactants. This viscosity effect may be even more pronounced in our extremely viscous graft copolymers.

#### Viscosity of HS-PAN-1:1

The plot of dispersion viscosity vs. pH for Prep. 3 (Fig. 1) gave a curve which was typical for all HS-PAN-1:1 products. Maximum viscosity was

attained in each case at the neutralization point which was pH 8.5 (Fig. 2). Although viscosity is greatly reduced below pH 4 and above pH 12, about 90% of the maximum viscosity is retained between pH 5.5 and pH 11. Variations in viscosity of HS-PAN with pH are typical of polyelectrolytes and undoubtedly due to counter-ion effects.<sup>17</sup> Prep. 1 (Table II) prepared under the mildest conditions exhibited the highest viscosity; however, it had the lowest carboxyl value and the highest nitrogen content. The comparatively high viscosity of Prep. 1 conceivably can be explained in terms of crosslinking either through possible azomethine linkages as postulated by Schurz<sup>18</sup> or through naphthyridine-type structures involving neighboring PAN chains, which are not as easily disrupted at lower base concentrations.

TABLE II  
Viscosities<sup>a</sup> of HS-PAN-1:1 Dispersions<sup>b</sup>

Dispersion, %	Prep. 1, cp	Prep. 2, cp	Prep. 3, cp	Prep. 4, cp
1.0	26,500 <sup>c</sup>	17,000	19,000	15,000
0.50	15,000	8,500	10,000	7,500
0.250	9,400	4,400	5,450	4,200
0.125	5,000	2,700	3,350	2,650
0.063	2,400	1,340	2,000	1,500
0.032	300	500	950	700

<sup>a</sup> Viscosities of all dispersions except that of Prep. 1 at the 1% level were determined at 25°C with a No. 4 spindle at a shear rate of 30 rpm.

<sup>b</sup> Dispersions had pH's of 8.5.

<sup>c</sup> Value obtained by extrapolation from plots of viscosities at 30 and 12 rpm for varying concentrations of Prep. 1.

Below the 1% dispersion levels, viscosities of most high-viscosity gums decrease rapidly in a nonlinear relationship with concentration. For HS-PAN, however, an almost linear relationship exists between viscosity and dispersion concentration from 1 to 0.063% with the exception of Prep. 1. The viscosity of Prep. 2 falls off rapidly in going from 0.063 to 0.032% concentration, whereas the viscosities of Preps. 3 and 4 decrease about 50%.

#### Effect of Salt on Dispersion Viscosities of HS-PAN-1:1

Decreases in dispersion viscosities of HS-PAN-1:1 products on addition of salts (pH 8.5) are undoubtedly due to counter-ion effects. At 1% concentration (Table III), significantly more viscosity is retained by Preps. 2, 3, and 4, however, than by Prep. 1. Dispersions of Prep. 3 retained more viscosity than the others upon addition of increasing amounts of KCl. The effect that KCl has on the viscosity of each preparation is most pronounced at the 0.5 and 0.25% dispersion levels. Also at these levels, relative differences in the abilities of the dispersions to retain viscosity are most pronounced. These differences undoubtedly reflect varying condi-

TABLE III  
Effect of KCl on Viscosities<sup>a</sup> of HS-PAN-1:1 Dispersions<sup>b</sup>

Dis- persion, %	KCl, %	Prep. 1 cp	Prep. 2, cp	Prep. 3, cp	Prep. 4, cp
2	8	—	14,000	15,300	—
1	0	26,500	17,000	19,000	15,000
	1	9,800	10,000	11,000	9,400
	2	6,800	6,900	8,900	5,800
	4	2,400	4,100	7,000	4,900
	8	1,100	3,000	5,000	3,600
0.5	0	15,000	8,500	10,000	7,500
	1	1,260	900	1,960	1,500
	2	260	442	1,000	1,170
	4	95	146	520	470
	8	50	110	240	280
0.25	0	9,400	4,400	5,450	4,200
	1	240	25	765	270
	2	10	—	180	80
	4	—	—	100	35

<sup>a</sup> Viscosities of all dispersions except that of Prep. 1 at the 1% level were determined at 25°C at a shear rate of 30 rpm.

<sup>b</sup> Dispersions had pH's of 8.5.

tions of preparation. Dispersions of Prep. 3 still exhibit significant viscosity at the 0.25% level in the presence of 4% KCl.

Trivalent cations suppress dispersion viscosity more than divalent ones, which in turn suppress viscosity more than monovalent cations (Table IV). In line with its behavior toward KCl, Prep. 3 appears capable of retaining more viscosity than the others in the presence of each of several different salts. Unexpectedly, the viscosities of Preps. 2 and 3 in the presence of 0.1% CaCl<sub>2</sub> and Mg(HCOO)<sub>2</sub> increased in viscosity; however, addition of more salt decreased viscosity. The initial increase in viscosity may be due to a few crosslinks introduced by carboxylic acid salt formation and the subsequent decrease in viscosity on addition of more calcium and magnesium ions is probably due to counter-ion effects and partial insolubilization by increased crosslinking.

#### Effect of Heating on Dispersion Viscosities of HS-PAN-1:1

Effects of heating on viscosities of HS-PAN-1:1 in 1% dispersions and then cooling to 25°C are illustrated in Figure 4. Dispersions of Preps. 2, 3, and 4 had excellent stability to heat up to 80°C although some viscosity was lost at 100°C. The dispersion of Prep. 1 was the most sensitive to heat although after heating it at 100°C viscosity measured at 25°C was still higher than the others.

#### Comparison of Viscosities—HS-PAN and Components

The grafting of acrylonitrile onto starch gives a copolymer whose hydrolyzed product exhibits markedly improved properties over dispersions



consisting of its nongrafted component parts (Fig. 5). PAN obtained from S-PAN-1:1 by acid hydrolysis was base-hydrolyzed under conditions similar to those employed to make Prep. 3. Theoretically complete hy-

TABLE IV  
Effect of Salts on Viscosities<sup>a</sup> of 1% HS-PAN-1:1 Dispersions<sup>b</sup>

Salt	Salt conc., %	Prep. 1, cp	Prep. 2, cp	Prep. 3, cp	Prep. 4, cp
NaCl	0	26,500	17,000	19,000	15,000
	1	10,800	6,200	10,000	6,600
	2	6,350	4,800	7,300	3,480
	4	2,340	2,550	6,300	3,480
	8	1,270	1,600	3,900	2,520
Li <sub>2</sub> SO <sub>4</sub>	1	11,300	9,350	9,600	8,800
	2	6,800	5,800	7,900	5,050
	4	3,000	3,350	6,500	3,700
	8	1,400	2,050	4,500	2,730
NaH <sub>2</sub> PO <sub>4</sub>	1	15,000	9,200	12,400	9,050
	2	11,100	5,900	7,000	6,100
	4	7,600	3,500	5,800	3,750
	8	1,400	1,700	4,200	2,760
NH <sub>4</sub> OAc	1	9,000	11,500	12,200	6,650
	2	5,200	4,500	6,500	6,050
	4	2,800	2,400	4,450	5,310
	8	900	1,200	2,700	2,120
NaOAc	1	12,800	10,300	10,500	10,200
	2	9,400	8,200	9,400	7,300
	4	3,260	5,300	6,450	4,450
	8	800	3,000	3,240	3,760
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	1	17,600	11,500	13,000	9,550
	2	14,400	9,600	10,700	8,000
	4	11,300	7,600	9,500	7,150
	8	8,000	7,000	9,200	6,550
CaCl <sub>2</sub>	0.1	18,800	20,000	22,100	9,200
	0.2	11,800	11,700	10,800	5,600
	0.3	2,000	2,300	6,250	2,800
	0.4	—	—	520	300
Mg(HCOO) <sub>2</sub>	0.12	18,500	19,100	21,100	12,100
	0.24	11,800	8,200	9,200	6,150
	0.48	3,000	2,100	2,860	3,550
	0.60	300	400	570	325
AlCl <sub>3</sub>	0.03	—	16,000	—	—
	0.06	16,500	14,500	15,500	10,100
	0.09	—	12,300	—	—
	0.12	11,400	11,000	12,100	7,300
	0.18	2,500	2,560	10,300	5,100

<sup>a</sup> Viscosities were determined at 25°C at a shear rate of 30 rpm.

<sup>b</sup> Initial dispersions had pH's of 8.5.

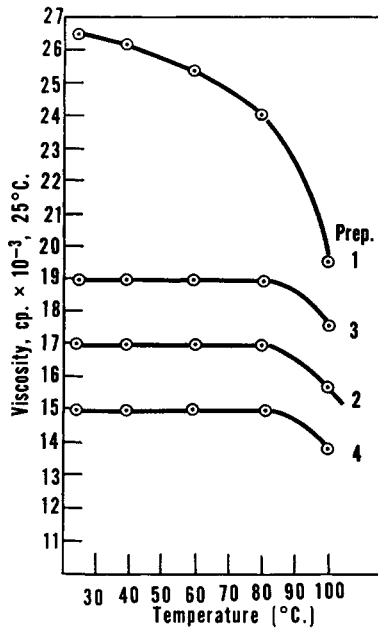


Fig. 4. Viscosity of 1% dispersions of HS-PAN-1:1 at 25°C after heating to various temperatures for 1/2 hr.

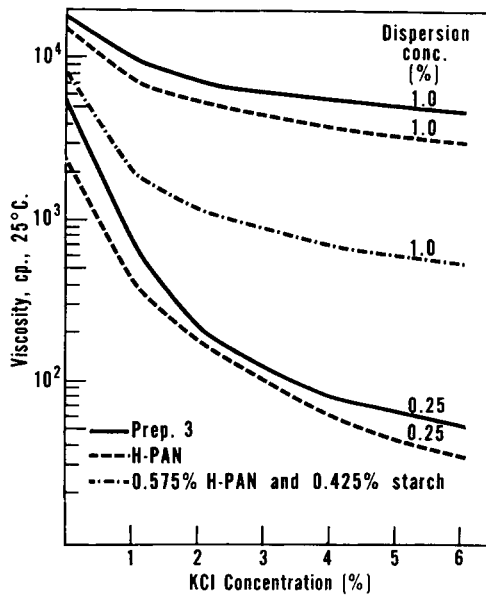


Fig. 5. Dispersion viscosities of Prep. 3, hydrolyzed polyacrylonitrile (H-PAN), and a mixture of H-PAN and starch.

hydrolysis of nitrile in S-PAN-1:1 to carboxyl groups should yield a product containing 57.5% grafted polyacrylic acid. Hence differences in viscosities of a 1% dispersion of HS-PAN-1:1 and a dispersion consisting of 0.575% H-PAN and 0.425% gelatinized starch may be regarded as an approximate measure of viscosity effects derived through grafting. A comparison of viscosities in the absence of KCl suggests grafting is responsible for a 2.5-fold increase in viscosity. The unusually high viscosity of HS-PAN-1:1 is undoubtedly due to an unusually long "effective chain length" created as a result of grafting.

Comparison of viscosities in the presence of 6% KCl indicates grafting is responsible for increasing viscosity by approximately tenfold. The more pronounced effects in the presence of KCl may be due to the nonionic character of starch.

When pure H-PAN is compared with HS-PAN, differences in dispersion viscosities are not so great; but, in the absence of KCl, the hydrolyzed graft copolymer, Prep. 3, is still about 60 and 100% more viscous at the 1.0 and 0.25% concentrations, respectively, than H-PAN.

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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