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FIBROUS PROTEIN FROM COTTAGE CHEESE WHEY

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee

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June 1974

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ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation and gratitude to Dr. H. O. Jaynes for his invaluable guidance and advice throughout the author's study at the University of Tennessee.

Sincere appreciation is expressed to Drs. B. J. Demott, W. W. Overcast, J. T. Miles, D. O. Richardson and J. L. Collins for their valuable guidance and criticism during the preparation and development of this study.

Due acknowledgment is made to Dr. M. Carter for making U. S. D. A. Textile Laboratory facilities available.

I am deeply greatful to Dr. E. A. Childs for his review and criticism of the manuscript and for his encouragement, advice and guidance along the study.

ABSTRACT

The possibility of making protein fibers from whey protein concentrate (WPC) prepared from cottage cheese whey by a polyphosphate complexing process was investigated. WPC prepared and used in fiber formation studies had a low lactose (2.67 percent) and reasonably high protein (70.78 percent) content. Fiber formation was studied by a wet-spinning process. Spinning solutions used were either aqueous alkaline WPC dispersions or aqueous alkaline WPC-anionic detergent solutions. Spinning solutions were extruded into a coagulating bath containing 12 percent glacial acetic acid and 12 percent NaCl on a weight basis.

Continuous fibers produced from aqueous alkaline WPC dispersions were not strong. Twelve and 14 percent aqueous alkaline WPC-detergent solutions containing equal concentrations (based on weight of WPC) of detergent, sodium lauryl sulfate (SLS) or sodium dodecyl benzene sulfonate (SDBS) in the presence of 0.5 percent β-mercaptoethanol formed continuous fibers with excellent handling properties. Detergent then was extracted with 60 percent aqueous acetone or 60 percent aqueous acetone containing 5 percent KCl.

WPC-detergent fibers put in water before the extraction of detergent disintegrated whereas detergent extracted fibers were not affected by boiling in water for 30 minutes. The average water absorption of detergent extracted fibers was 1.23 times the dry weight. Tensile strength and elongation of detergent extracted fibers were significantly ($P<0.05$)

affected by the stretching operation. Tensile strength was increased and elongation was decreased.

Time elapsed up to 24 hours between the preparation of the spinning solutions and fiber production did not result in a decrease in the protein content of detergent extracted fibers. Presence of KCl did not enhance the detergent extracting capacity of 60 percent aqueous acetone. However, acetone treatment removed most of the detergent. Overall mean composition of WPC-SDBS fibers was 98.5 percent protein, 0.6 percent SDBS, and 1.0 percent phosphate, whereas, WPC-SLS fibers contained 92.6 percent protein, 1.3 percent SLS and 1.2 percent phosphate.

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CHAPTER I

INTRODUCTION

Protein deficiency has become an alarming nutritional problem throughout the world, yet the population of the world is expected to exceed six billion by the end of the century. In the last decade, the concern about finding ways to efficiently provide more protein foods has grown remarkably.

Traditionally some thirty-four million tons of fluid whey annually produced by cheese plants around the world (19) has been treated as a waste product, resulting in the loss of a considerable amount of high quality protein (173,174,176). With rising emphasis on the need to reduce environmental pollution (51,109,158) processing whey only for disposal purposes has become impractical. For all those reasons, efforts now are directed toward the utilization of whey. Most researchers have been concerned with the development of commercially feasible processes to separate proteins from other whey constituents and then to produce an undenatured whey protein concentrate (WPC) that can be incorporated into foods for human consumption. WPC's produced by reverse osmosis (54,62,108,109,133,158), ultrafiltration (54,109), electrodialysis (43,59,60,123,167) and polyphosphate complexing (76,83,93,94) have been tested.

In addition to WPC, a number of high protein products are presently available from a variety of sources including soybeans, cottonseed, leaf, sunflower, peanut, fish and microorganisms (20,45,47,65,137,146,153,169).

Protein concentrates or isolates will not be a valid answer to protein deficiency problems unless they are converted into a form which people will buy and eat (67). Converting the protein material into fibrous form and utilizing the resulting fibers in the fabrication of masticatory foods has been a promising approach to improve the acceptability of non-meat proteins (73,87). Total sales of fabricated foods in 1972 were $13 billion and are projected to exceed $23 billion by 1980, whereas the sales of the substitutes for meat are expected to reach $11 billion in 1980 from $2 billion in 1972 (11).

In this study an attempt was made to investigate the factors involved in making protein fibers from WPC prepared from cottage cheese whey by a polyphosphate complexing process.

CHAPTER II

REVIEW OF LITERATURE

1. RECOVERY OF WHEY PROTEINS WITH LINEAR POLYPHOSPHATES

Complex formation between proteins and polyelectrolytes has been long utilized to recover proteins from various sources (68,74,81,82, 115,152,153,154). All phosphates have the properties of highly charged anions and thus exhibit the properties of typical polyelectrolytes (50).

Proteins are precipitated by polyphosphates under acidic conditions (50,68,105,154). Polyphosphates interact with the cationic sites on the proteins with a stoichiometry consistent with the law of mass action (30). This conclusion was supported by observations indicating that during the course of protein-polyphosphate complex formation milk proteins behaved as multivalent cations, and a complete displacement of sodium from the polyphosphate took place (162).

Evidence concerning the specific nature of interaction between milk proteins and polyphosphates has been reported. Vujicic and DeMan (163) analyzed the filtrates of sodium hexametaphosphate (SHMP) milk protein suspensions by paper chromatography and demonstrated that the polyphosphate remained in the precipitated fraction. In gel electrophoretic studies, the polyphosphate-protein complex migrated toward the anode which suggested to Melynchyn and Wolcott (114,116) that the negatively charged phosphate group was bound by the proteins. Their conclusion was

further supported by Poulic's (132) findings that SHMP had no apparent effect on any of the caseins or whey proteins in alkaline buffer. Others (50) thought that the acidic polyphosphate anions formed ionic linkages with the basic amino groups of the protein molecules, thereby lowering the net charge and causing precipitation. Factors found to affect complex formation and precipitation of proteins by polyphosphates included chain length and concentration of polyphosphate, pH and ionic strength (105,113,127). However,the exact interaction of these factors has not been clearly demonstrated (116).

Methods for preparation of WPC by complexing and precipitation with polyphosphates have been developed empirically. The recovery of whey proteins with polyphosphates was first studied by Gordon (69) who precipitated the proteins at pH 3.0 with 0.2 percent (w/v) SHMP. The precipitate was isolated by either filtration or centrifugation. A 91 percent protein recovery was reported by Hartman (75), and Hartman and Swanson (76) at pH 2.5 using 0.5 percent (w/v) SHMP. According to Hidalgo et al. (83) maximum precipitation occurred at pH 3.0 with SHMP. Concentration of SHMP required for maximum precipitation from acid and rennet wheys were 0.1 and 0.07 percent (w/v), respectively.

Gel electrophoretic studies by Jones et al. (93,94) on protein-ferripolyphosphate complexes obtained from cottage cheese whey indicated that β-lactoglobulin was precipitated primarily at low polyphosphate concentrations between pH 3.2 and 4.0 while α-lactalbumin was precipitated primarily at high polyphosphate concentrations at same pH. On the other hand Melachouris (113) noted an increased precipitation of pure β-lactoglobulin with increasing concentrations of SHMP between pH 2.0 and 4.0.

He observed also an increased precipitation with longer polyphosphate chain length. However, the precipitation was independent of chain length at high protein concentrations. Temperatures between 5°C and 73.5°C were not significantly different as related to precipitation but increased ionic strength markedly reduced precipitation. The mineral composition of whey was found to have a strong influence on the protein polyphosphate interaction, causing large differences in protein recovery among different whey samples (83). Hidalgo et al. (83) precipitated over 90 percent of the protein of whey with SHMP after decationization. However, Pallansch (129) reported that SHMP precipitated all but the immunoglobulins of whey.

Studies in which proteins were recovered by combining SHMP precipitation with column chromatography (172), gel-filtration (83,166) or ion-exchange (166) have been described. Webb (166) increased the protein content of WPC to 80 percent, and Hidalgo et al. (83) 88 to 90 percent by gel filtration. Gel-filtration was reported to remove mainly lactose while ion-exchange removed most of the phosphate (83).

2. COMPOSITION AND PROPERTIES OF WHEY PROTEIN CONCENTRATE

Presently, WPC does not have an established composition. Comparative studies on the chemical analysis and properties of WPC prepared by various processes are also very limited. Table I shows the distribution of protein, ash, lactose, fat and moisture in WPC manufactured by several methods.

TABLE I

CHEMICAL COMPOSITION OF WPC PREPARED BY VARIOUS PROCESSES

Process	Protein	Lactose	Ash	Fat	Moisture	Reference
			%			
SHMP-Complexing	55.7	13.0	13.7	5.3	-	(123)
	72.0	12.0	-	-	-	(83)
SHMP+Gel-filtration	78.7	2.9	13.7	-	1.9	(166)
	77.1	2.9	13.5	-	1.9	(167)
CMC[a]-complexing	49.8	20.1	8.0	12.0	-	(123)
Reverse osmosis	35.0	51.4	4.3	2.2	4.0	(166)
	21.1	67.5	6.2	-	-	(176)
Ultrafiltration	56.8	27.2	3.4	4.8	-	(123)
	55.6	27.2	3.7	0.9	5.3	(167)
Electrodialysis	28.0	51.0	10.0	1.3	4.0	(167)
	32.9	51.8	9.0	3.3	-	(123)
	35.0	50.0	3.0	3.5	5.0	(43)
Dialysis	66.0	26.2	2.0	2.0	-	(123)
Gel-filtration	72.5	8.3	5.4	5.2	-	(80)

[a]Carboxymethylcellulose.

According to Morr et al (123) the need for having WPC and having it in an undenatured state was obvious for two reasons: First, the protein concentration in dried wheys was so low (36,107), that the amount of protein which can be incorporated into food formulations was limited by high lactose and ash content (122). Secondly, the least expensive method of preparing WPC, heat coagulation, yields a product that has only limited use in the manufacture of foods due to its insolubility and gritty character (122,173,174).

SHMP-complex WPC was reported to have poor solubility at pH 3.0 and 4.0 (83,123). In fact, 9 percent residual SHMP in WPC has been reported even after gel-filtration and ion-exchange (83). Thus, the reliability of assessing the solubility of SHMP-complex WPC at pH 3.0 and 4.0 was questioned (123).

The solubility of SHMP-complex WPC proteins was found to be highly pH dependent with solubilities of 31.1 (pH 2.0), 73.1 (pH 6.0) and 85.9 (pH 8.0) percent (122,123). Similar results were reported by Hidalgo et al. (83) who found a 90 percent solubility at the isoelectric zone (pH 5.0 and 6.0), and suggested that SHMP-complex WPC protein was in its native state at pH 5.0 and 6.0.

The swelling behavior of gel filtration WPC containing 75.2 percent protein on a dry basis was studied by Hermansson (80), and compared to that of sodium caseinate and Promine-D (soy protein concentrate). Despite a 89.3 percent solubility at pH 7.2, aqueous solutions of WPC exhibited poor swelling ability (about 1.5 percent, measured as ml water uptake per g of WPC) over a range of pH's (4.0 to 10.0), ionic strengths (0.2

Dry spinning involved dispersing the polymer in a suitable solvent and extrusion in the dispersed state (63,145,171). The solvent was then removed by evaporation (145). This process was limited to those polymers which were soluble in volatile solvents (140).

Wet-spinning also consisted of extrusion in the dispersed state (84,131,134). A number of sequential operations were involved in the manufacture of fibers from natural and synthetic polymers by wet-spinning (178). Preparation of spinning solution called "spinning dope" was the first step (52). The second step, the spinning process, consisted of extrusion of spinning solution into a liquid non-solvent coagulating bath through small orifices (dies, spinnerets) and solidification of polymeric material into fibers in the coagulating bath (26,28). In the third step fibers were subjected to a stretching operation and collected on a suitable mechanical device (178). Then, fibers were treated to improve their properties.

All three processes have been widely used in the textile industry while only wet-spinning has found applications in the food industry.

The internal and external structure of wet spun-fiber is determined by the entire spinning process. However, each step in the process affects different aspects of fiber structure (178).

The rheology of the polymer solution was an essential part of the spinning process. Rheology, defined as "the science of the deformation of matter" (61,78), derives relationships occuring between stress in a material subjected to deformation and deformation conditions. Certain material characteristics, including viscosity and relaxation time, aided

in predicting the flow behavior of spinning solutions (178). Viscosity was a critical factor in wet-spinning since it determined the force necessary to pump the spinning solution through filters and spinnerets (140,145). According to Fox (58) viscosity arose from the frictional interactions of one "segment" of a polymer chain as it moves relative to its neighbors and from interaction between units joined by primary valence bonds into long chains and by "entanglements" into larger network structures. Viscosity decreases with temperature (140,178) and increases with polymer concentration and polymer molecular weight (140, 145). The highest viscosity attainable short of gel formation was found to give the best spinning conditions (145).

A spinning solution must be stable, yet "spinnable", under the conditions of the spinning operation. Spinnability was conventionally defined by Ziabicki (178) as "the ability of a liquid to form long continuous liquid threads." Ferguson and Ibrahim (55) described the "spinnability range" as "the highest extrusion velocity at which the production of a homogeneous fiber of good quality could still be maintained." Spinnability has been measured by determining the maximum thread length (178).

Several attempts have been made to determine the conditions essential for spinnability. Surface tension and viscosity were considered to be critical (86,178). Ziabicki (178) followed the physical processes leading to the fracture of liquid threads by high speed photography and showed the existence of two different break mechanisms. The first mechanism, capillary break-up, was related to surface tension. When a

polymer solution was extruded through a spinneret, a large, new interface was created. Surface forces operating at the interface made the cross-section of a fiber tend toward a circular shape regardless of the shape of the orifice. These surface forces also made any globe of a liquid unstable (became greater in length than in circumference) and the globe tended to break into drops (140). When spinning solutions of low viscosity were used, this mechanism manifested itself (178). In the second mechanism, cohesive break-up, the determining factor for break up was the tensile strength of the liquid. This mechanism was expected when polymers with high molecular weight or excessive branching were used (178).

The shear flow which takes place in the spinneret channel determined the parameters of the first step of the spinning process, extrusion (178). Orifice geometry was reported to have little effect on the formation and the properties of fibers since these characteristics appeared in a region relatively distant from the spinneret face (42). However, geometry of the spinneret channel was found to be critical because it provided specificity to the flow (178).

Under conditions of wet-spinning, the polymer solution was usually alkaline while the coagulating bath was acid. Negatively charged particles of the bath were deposited on the positively charged face of the spinneret and even in the spinneret orifices. Similarly, positively charged colloid particles in the polymer solution were deposited in the innerface of the spinneret (140). These blockages could cause a breakdown of the spinning operation. Despite such remedies as the use of

glass spinnerets or the polarization of the spinneret face, the polymer solution still spread over the spinneret face unless fibers were pulled away from the spinneret (140). The addition of surface active agents such as cation active agents to the coagulating bath has been successfully used to prevent a breakdown of the spinning process (104,140).

When the spinning solution emerged from the spinneret, it immediately tended to relax since the shearing force had been removed (55). Most relaxing polymer solutions tended to increase their diameter, and this was called "die swell" (178). The amount of die swell has been shown to decrease with increasing capillary length (55).

Concurrent with relaxation, the spinning solution began to extend and coagulate. The coagulation process precipitated the spinning solution and extension caused molecular orientation to occur (55,178). If coagulation proceeded faster than the relaxation time then the molecules were coagulated in the fiber in a more axially oriented form than they would have been if relaxation was complete before coagulation (55).

Several processes may proceed simultaneously during coagulation, such as osmosis of the solvent, diffusion of coagulating bath components into fibers, chemical reactions between diffusing substances and the polymer molecules, salting out effects and electrolytic effects (140). When the spinning solution was brought into contact with the coagulating bath, a diffusional interchange took place between the two phases, and the spinning solution solidified (130,131). The mechanism of diffusion during the coagulation step of wet-spinning is not yet completely understood (17,131). To obtain fundamental information, Paul (130) studied

diffusion in model static experiments. He observed a distinct boundary associated with coagulation when gelled rods of spinning solution were immersed in a coagulating bath. He measured the depth of penetration of the coagulating bath into gelled rods at various time intervals and found a linearity between the rate of penetration and the square root of time.

Rapid desolvation of the polymer accompanied by a rapid coagulation rate during spinning resulted in the formation of a well defined "outer skin" on the fiber (140). A rigid skin could prevent further coagulation of the fluid core of the fiber (37).

Total stretch of fiber produced by wet-spinning has been shown to be a function of the relative speeds of extrusion and collection (139, 140). However, the force required to continuously take up fibers on a collection device had to overcome a number of resistances (38,140):

1. Internal friction forces due to viscosity of spinning solution (140).
2. Surface tension forces due to creation of a new fiber surface (37,38,140,178).
3. Hydrodynamic drag caused by the relative motion of the moving fiber and the coagulating bath (37,140).
4. Friction drag at the guides over which the fiber passes (140).

Resistance to stretch increased with the rate and progress of coagulation (38). Thus the degree of stretch was significantly affected by the composition of the coagulating bath (38) and conditions of coagulation (140).

Stretching causes the parallelization and extension of structural units along the fiber axis known as "orientation" (178). Those regions of fibers where polymer molecules were not only oriented linearly but arranged also in full three dimensional order were referred to as "crystalline" (33), and those with complete disorder were called "amorphous" (1,117).

Although reference has been made to orientation during the relaxation, most of the orientation actually occurred during stretching (34). When a fiber was oriented by stretching, because of improved alignment of molecules parallel to the fiber axis the molecules were able to pack themselves in a more orderly manner and the fiber became more crystalline (120). As a result of improved packing there was more opportunity for inter-atomic attractive forces (e.g., hydrogen bonding) to be exerted. Individually these were like weak cross-links, but together they caused a large increase in the strength of the fiber (120).

4. SPUN PROTEIN FIBERS

Fibers differ widely in their origin and uses which necessitates their classification. Conventionally, fibers have been divided into two broad categories; "natural" and "man-made" (9). Authorities in the fiber field generally have recognized two distinct classes of man-made fibers: "artificial fibers", made from natural polymers,and "synthetic fibers", made from wholly synthetic polymers (9,39,179). Man-made protein fibers were included in the artificial fibers. However, three terms, "artificial", "synthetic" and "regenerated" have been used interchangably to

refer to man-made protein fibers (16,104). Man-made protein fibers prepared by the wet-spinning process were called "spun protein fibers" (73).

The possibility of producing man-made protein fibers was predicted by the Chinese in 2640 B.C. (23). The idea was repeated throughout the history by many scientists including Robert Hooke who suggested the production of fibers from natural polymers (98,104,139,179). However, the first known attempt to make protein fibers was the production of gelatinous fibers in 1894 (23), and in 1935, a casein fiber called "lanital" was introduced to the textile industry (23,139). Subsequently attempts have been made to produce protein based man-made fibers for textile uses. Peanut protein (153), casein (111,135) and zein (121) fibers were produced on a commercial scale in the United States between 1935 and 1945 (153).

Although earlier uses of man-made protein fibers have been directed at textile applications, Boyer (26) in 1954 brought the wet-spinning method into the food industry when he prepared edible soy protein fibers. Subsequently, fiber spinning in the food industry was improved to a continuous process (73,168). Today, preparation of edible spun protein fibers follows in general the principles and operations of the wet-spinning method discussed earlier. Modifications and other considerations have been disclosed in patents issued for manufacturing edible fibers from casein (22,28,39,66), soy protein (12,26,27,28,49,66), peanut protein (12,66) and safflower seed protein (52). Recently, spun protein fibers from single cell protein (SCP) also have been reported (87).

In spite of promising success achieved in the preparation of edible spun protein fibers, most of the developments have been based on empiricism. Very little work has been published with respect to what specific properties determine the suitability of a protein as a fiber raw material. However, studies with other systems indicated that, to be a fiber former a given protein molecule must be linear, have a high degree of symmetry and be able to conform to a system of parallel chains (84, 91,104). The presence of bulky side groups in the protein molecule was believed to impair the strength and other properties of fibers by preventing close packing and crystallite formation (120,134).

The molecular weight of protein, in its dispersed state, should not be less than a minimum value (23,106). Lundgren (104) reported that the minimum degree of polymerization (DP) required for fiber formation was somewhere between 40 and 80 which corresponded to molecular weight of 10,000 for an average polypeptide chain. Fibers from substances of smaller molecular weight would not be expected to have much strength. The strength of fibers increased with an increase in molecular weight up to 24,000 (200 DP) and reached a limiting value between 36,000 and 72,000 (300 and 600 DP).

The protein had to be completely dispersible in a suitable solvent (164). The indispersible protion of the protein was thought to have an adverse effect on the fibrous character of the network (134). Insoluble non-protein components of the protein molecule were also believed to have such an effect (134). According to Walker (164), the manner in which a commerical process has been developed for making fibers from a

known polymer was entirely dependent upon finding a suitable solvent. Although several solvents have been used for preparing spun protein fibers (70,71,100,101,102,103,112), aqueous sodium hydroxide solutions have been the only preferred dispersing medium for making edible spun protein fibers (12,27,52,96,97,159,168). Sodium hydroxide, which converts proteins to unfolded and dissociated polypeptide chains (95, 104, 155), served also to adjust the pH of the dispersion (17). Unfolding and dissociation evidenced by an increase in viscosity which the protein underwent when exposed to strong alkali and by a shift in the sedimentation behavior of the protein components (95,104). Table II indicates that a variety of spun protein fibers have been prepared with spinning solution satisfying a range of conditions.

Circle et al. (39) studied the rheology of soy protein (Promine-D) dispersions and observed that at room temperature apparent viscosity of dispersions rose exponentially with increase in concentration. Similar results were obtained by Kelley and Pressey (95) who noted that the concentration of soy protein determined the shape and magnitude of the viscosity curves as well as the time at which soy protein dispersions reached maximum viscosity. They found also that the concentration of the sodium hydroxide during the preparation of the spinning solution governed the practical limits within which the protein content could be varied.

The increase in viscosity of 10 percent soy protein dispersions with increase in pH up to pH 9.0 was attributed to enhanced solubility of soy protein components (39). Ultracentrifugal analysis of spinning solutions

TABLE II

SPINNING SOLUTIONS PREPARED WITH VARIOUS PROTEINS FOR THE PRODUCTION OF EDIBLE SPUN PROTEIN FIBERS

	Spinning Solution						
Protein Source	Solvent (Aqueous NaOH) (%)	Concentration of Protein Source (% w/w)	Concentration of NaOH (%)	pH	Temperature °C	Viscosity (Poises)	Reference
Casein	10	20-24	4-5	a	70	a	(27)
Soybean flake	10-20	15-30	b	11.5-13.5	a	a	(168)
Soybean protein isolate	b	18	7.0	a	40	200	(97)
Soybean protein[c]	5-10	10-30	b	9.0-13.5	45	100-200	(96)
Casein + Soy flour (50:50 w/w)	5	27	0.7	8.5-9.3	45	a	(159)
Safflower seed meal	10	20-30	5.0	9.0-13.5	45	50-1000	(52)
Peanut protein concentrate	b	19	b	10.8-12.3	a	a	(12)

[a]Not reported.

[b]Solvent used was NaOH, but the concentration was either not reported or the procedure described did not lend itself to calculation.

[c]Protein source was not further specified.

indicated the presence of all major soy protein components, even at pH 11.0 (95).

Addition of disulfide cleaving agents such as sodium sulfite (39, 95) and cystein-hydrochloride (39) at low concentrations markedly reduced the viscosity of soy protein dispersions. Another disulfide cleaving agent, 2-mercaptoethanol, increased the solubility of soy protein components, thereby caused changes in the sedimentation behavior (95).

DeGroot and Slump (48) studied the effect on amino acid composition and nutritive value of proteins (casein, soy protein isolate, sesame protein, and coconut protein) produced by exposing them to strong alkali under varying conditions of pH, temperature and time. Exposure of proteins to sodium hydroxide at pH 12.2 resulted in the formation of the amino acid derivative lysinoalanine (LAL) which was poorly absorbed by rats. The amount of LAL formed in soy protein isolate increased with increase in exposure time and temperature. The presence of LAL was accompanied by decreased contents of lysine and cystine and decreased net protein utilization (NPU). The decreased NPU of alkali treated soy protein isolate could not be alleviated by amino acid supplementation.

The coagulating baths generally contained an acid constituent and were preferably an aqueous solution of a salt and an acid. Coagulating baths containing lactic acid and sodium chloride (52,97,159) or glacial acetic acid and sodium chloride (12) have been used more frequently than others, such as baths prepared with calcium chloride and hydrochloric acid (15). Neither salt nor acid concentration of the coagulating bath has been found to be critical (12,96). Sodium chloride has been used

in varying concentrations from 0.5 percent to 16 percent (w/v) and acid concentrations from 0.5 percent to 10 percent (w/v) (12,52,96,168).

Spinnerets used for extrusion were similar to those employed in the textile industry. A spinneret was actually a small die having many holes, each being from 76 to 90 microns in diameter (12,28,49,52,96).

Stretching was usually accomplished by passing a continuous bundle of fibers over a series of rolls revolving at increasing speeds (26,52). The amount of stretch that could be given to protein fibers for obtaining the maximum strength and elasticity was limited by the optimum amount of orientation attainable for each type of protein (26,111). Stretching tensions ranging from 50 to 400 percent (26,27) and from 100 to 200 percent (52) have been applied with soybean and safflower protein fibers, respectively.

Boyers (26) observed that the texture and chewability of spun protein fibers were directly affected by the orientation in the protein molecule. Stretching procedures involving no more than leading the fibers away from the extrusion orifice at a rate of speed sufficiently great to prevent the fibers from being formed in a kinky condition enhanced the orientation and consequently, the strength of fibers.

Texture of fibers has been controlled by soaking them in a treatment bath containing suitable reagents. Treatment baths containing sodium chloride from 0.5 to 12 percent (w/v) were found to have a toughening effect on fibers (26). The degree of toughness has been controlled by adjusting the pH (4.0 to 7.0) and temperature (29 to 38°C) of the salt solution in which the fibers were slowly agitated for a sufficient period

of time (28). At lower temperatures the fibers tended to be very brittle and to break upon agitation. At pH values below 4.0 fibers were dry and tough. Variations in the pH of fibers permitted a variation in the moisture content, the higher pH values permitting the fiber to hold substantially more moisture.

Thorough studies concerned with further evaluation of textural and structural properties of edible spun protein fibers have not been reported. However, food products prepared with spun protein fibers and methods of manufacturing them have been reviewed in detail by Gutcho (73) and Noyes (128).

5. SOME PROPERTIES AND USES OF SYNTHETIC DETERGENTS IN FIBER STUDIES

Synthetic detergents have been classified generally as non-ionic, cationic and anionic according to the sign of the charge on the hydrocarbon group conferring surface activity upon ionization in water (52, 142). Anionic detergents comprised the largest group of synthetic detergents (46). Fifty-three out of 60 subgroups of anionic detergents consisted of sulfated or sulfonated products (151).

The existence of many synthetic detergents with potent biological properties has stimulated research on their interactions with proteins. Two classes of anionic detergents, alkyl sulfates and alkyl benzene sulfonates have been studied widely (57,59,142,157). The most frequently investigated synethetic detergent, sodium lauryl (dodecyl) sulfate, (SLS,SDS), is a mixture of sodium alkyl sulfates consisting chiefly of

of sodium lauryl sulfate (136). Similarly sodium dodecyl benzene sulfonate (SDBS) is a mixture of sodium alkyl benzene sulfonates consisting chiefly of sodium dodecyl benzene sulfonate.

Studies concerned with the viscosity, equivalent conductivity and osmotic coefficient of aqueous solutions of detergents indicated that they exist in solution both as single ions and as micelles (142,144). Monomers which take part in micelle formation were characterized by possessing two regions in their chemical structure. One was a hydrocarbon chain, the hydrophobic region of the molecule, and the other was an ionized group or water soluble group, the hydrophilic region of the molecule (53,142). This double nature was responsible for the properties of solubilization, surface activity and micelle formation (53). Micelle formation occurred above a certain concentration known as the critical micelle concentration (CMC), and was due to a decrease in free energy of the system (53,64,150).

Depending on the conditions of study, synethetic detergents were shown to produce diverse effects on proteins, including complex formation (124,125,126,142,149,160,161), denaturation (29,56,72,79,92,149) and precipitation (102,110,141,142,149). Complex formation of β-lactoglobulin with SLS (31,32,56,72,138,143,144) and SDBS (101,102) has been studied. Lundgren (102) showed by electrophoresis that β-lactoglobulin combined with SDBS in ratios corresponding to the total number of its basic groups. Hunter and McDuffie (88) noted the ability of reduced proteins to bind more SDS than their native counterparts. Pitt-River and Impiombato (138) demonstrated by equilibrium dialysis that the

failure to reduce disulfide bonds in β-lactoglobulin invariably resulted in lower binding of SDS to the protein. Reynolds and Tanford (143,144) have shown that a variety of reduced proteins including β-lactoglobulin bound identical amounts of SDS on a gram to gram basis. Their results indicated that the binding was a function of the free SDS concentration in solution and was independent of the numbers and the size of the SDS micelles present. They considered binding to be essentially hydrophobic in nature, but did not exclude ionic interactions. However, the nature of interactions may be more complicated since they almost certainly entailed strong binding all along the polypeptide chain regardless of the polarity of the side chains (77).

Groves et al. (72) determined the denaturation of β-lactoglobulin, measured as an increase in optical rotation and decrease in solubility, and found that β-lactoglobulin denatures in buffer solutions more alkaline than pH 8.0. Under similar conditions β-lactoglobulin in SDS solution denatured more slowly than did the native protein, suggesting that the presence of detergent increased the stability of β-lactoglobulin.

Hydrodynamic and other physical studies of protein-SDS complexes suggested a model of a thin rod of constant diameter and length proportional to the length of the protein chain of the complex (121,143,144). Dimensions were consistent with a helix like conformation with SDS molecules intercalated along the length of the helix (77). The extensive binding of detergent produced a strong solubilization effect since the highly charged surface of the protein-detergent complex tended to repel other polypeptide chains and prevent aggregation (77,102).

Changes in the diffusion and sedimentation behavior of proteins (100,102,142) and solubilization effects accompanied by enhanced viscosity were considered to indicate that the protein chains had unfolded. Measurement of relative viscosity of proteins in SDBS solution yielded viscosities higher than that of either constituent alone (101,103,142). Along with the change in viscosity a corresponding improvement in the spinnability of protein-detergent solutions has been observed (100,101, 102,103). Lundgren (100,101,102,103) utilized these observations in the production of textile fibers from spinning solutions of egg-albumin, soy protein and corn protein prepared with SDBS and SDS. Gould and Whittier (70,71) preferred either sodium salts of sulfonated vegetable oils (71) or SLS (70) in the production of textile fibers from casein. Moreover, Lundgren (101,102,103) noted the extraction of most of the detergent by 60 percent aqueous acetone, particularly in the presence of electrolytes.

6. SAFETY OF SODIUM HEXAMETAPHOSPHATE, SODIUM LAURYL SULFATE AND SODIUM DODECYL BENZENE SULFONATE

Sodium Hexametaphosphate

In common with all salts, excess quantities of linear polyphosphates would be expected to be toxic to an organism through their effect on mineral balance in the body and on osmotic pressure of the body fluids (50).

Ellinger (50) recently reviewed the use of phosphates in the food industry including their safety and regulatory aspects. Diets containing

1.8, 3.0 and 5.0 percent of SHMP were fed to rats. Slight increases in kidney weight and renal calcification were observed in a few rats on the 1.8 percent level, whereas, all animals showed kidney calcification on 3.0 percent and 5.0 percent levels. Dogs given a diet that contained increasing levels of SHMP from 0.1 g/kg/day to 4.0 g/kg/day for five months began to lose weight when the daily SHMP dose reached 2.5 g/kg/day or more. Reduced growth rate and protein efficiency ratio (PER) were observed when rats were placed on a diet containing 3.5 percent SHMP for five months. Autopsy and histological and chemical studies did not reveal any adverse physiological effect or any change in the utilization of calcium, phosphorous or iron.

In contrast to polyphosphates, which are acknowledged to precipitate calcium, Borenstein and Schwarts (25) found an increased absorbtion of calcium in rats when they had a diet to which 7.0 percent SHMP was added. They presented evidence also that SHMP was absorbed intact through the intestinal wall as SHMP-calcium complex, and after absorbtion, SHMP was hydrolized to orthophosphate.

The FAO/WHO Expert Committee on Food (177) has recommended that 30 mg or less phosphorous per kilogram body weight is to be considered safe under all conditions of diet and 30 to 70 mg of phosphorous per kilogram body weight when dietery calcium is high.

The U.S. Food and Drug Administration (FDA) accepted phosphoric acids and their calcium, potassium, sodium and aluminum salts as GRAS (Generally Recognized As Safe) (41). No limitations were set except that the amount added to food should not exceed the amount required to accomplish the intended purpose.

SHMP is the longest chain length polyphosphate allowed for use in meat products by the Meat Inspection Division of Consumer and Marketing Service of U.S. Department of Agriculture (40).

Detergents

The use of synthetic detergents for several non-detersive applications in medicine and in the cosmetic industry has increased within recent years. Purification of drugs, preparation of topical ointments, shampoos, skin lotion, formulation of antihelmintic preparations and treatment of peptic ulcer and ulcerative colitis are only some examples in which anionic detergents, particularly SLS, have been widely used (148,149). Concurrently, in industrialized countries the public health aspects of synthetic detergents with respect to internal consumption and possible increase in dermatitis have received increased attention (24). The Standing Committee on Synthetic Detergents in the United Kingdom reported that detergents had little effect on the incidence of dermatitis (24). In general, products of long, straight chain structure were less irritating than products of short, branched chain structure (149). Skin irritancy was especially specific for detergents containing high proportions of eight to ten carbon chains (147).

Studies concerned with possible harmful effects of contamination of foods with detergents through the practice of washing dishes with detergent formulations containing SLS and SDBS showed that less than 0.14 g total surfactants consumed yearly by one person in the foods eaten does not present any hazard to health (68). Human volunteers given 0.1 g

doses of alkyl benzene sulfonates daily for four months showed no ill effects (8). Daily ingestion of SLS or its introduction to duodenum over the range 0.2 to 0.3 g was not found to inhibit intestinal food absorbtion (148,149).

Burke et al. (35) identified liver by whole body autoradiography as the site of metabolism for alkyl sulfates. Daily dietary doses of 1,000 parts per million SLS were found to have no effect on rats during a 90 day feeding period (165). The LD_{50} values, the minimum dose required to kill 50 percent of the test animals, for detergents containing sulfates and sulfonates administered orally were in the range of 2 to 8 g per kilogram body weight (149). The Food Protection Committee of the Food and Nutrition Board (57) evaluated the safety of surfactants and concluded that there is no toxic effect common to all surfactants; thus the safety of each surfactant for use in foods must be evaluated separately. No evidence of carcinogenicity of SLS and SDBS has been reported (68).

Food uses of SLS and SDBS and the amounts permitted for use is shown in Table III.

TABLE III

USES OF SLS AND SDBS IN THE FOOD INDUSTRY

Detergent	Function and Use	Maximum Amount Permitted (%)	Reference
SLS	As an emulsifier in:	0.1	
	Egg white solids	0.1	(2,3)
	Frozen egg whites	0.0125	(2,3)
	Liquid egg whites	0.0125	(2,3)
	As a surfactant in:		
	Fumaric acid based acidulants for use in food	0.005 (in finished food)	(7)
	As a film former:		
	In formulations used for coating fresh fruits	minimum quantity to accomplish the intended use	(5)
	As a whipping agent:		
	In gelatine used to prepare marshmallows	0.5 (w/w)	(147)
SDBS	As an emulsifier in:		
	Washing fruits and vegetables	0.2 (in wash water)	(4)
	In the production of food contact articles added to polyvinyl chloride or vinyl chloride copolymers	2.0 (by weight of polyvinyl	(6,10)
	Hog scale agent: For removal of hair from carcass	in an amount sufficient	(147)

TABLE III (continued)

Detergent	Function and Use	Maximum Amount Permitted (%)	Reference
	Assists lye peeling of fruits and vegetables	-	(6,147)
	Prevents staining of exterior of cans	0.05 (in retort) water	(147)

CHAPTER III

MATERIALS AND METHODS

1. PREPARATION OF WHEY PROTEIN CONCENTRATE

A method outlined by Hartman and Swanson (76) for recovering whey proteins with polyphosphates was modified for this study. Fresh cottage cheese whey obtained from the Knoxville plant of Pet Milk Company was used for all WPC preparations. Sodium hexametaphosphate (Vitrafos) with a chain length of ten carbon atoms was used and was a gift of Stauffer Chemical Company, Westport, Connecticut. Whey was brought to room temperature and samples taken for protein determination. Then, WPC was prepared by the protocol outlined in Figure 1. With constant stirring, the whey was adjusted to pH 3.0 by the dropwise addition of concentrated hydrochloric acid. With continued stirring, 0.5 percent (w/v) SHMP was added as a freshly prepared, saturated polyphosphate solution.

The mixture was readjusted to pH 3.0 and stirring was continued an additional minute. After setting for two hours the liquid had separated into two phases. The top liquid was transferred into another container with a Masterflex-Tubing Pump (Model 3014, Cole-Parmer Instrument Co., Chicago, Illinois) and labeled as supernatant 1. The remaining protein slurry was centrifuged for 30 minutes at 810xg. This supernatant was mixed with supernatant 1 and the mixture labeled supernatant 2. A saturated polyphosphate solution was added to obtain a final SHMP

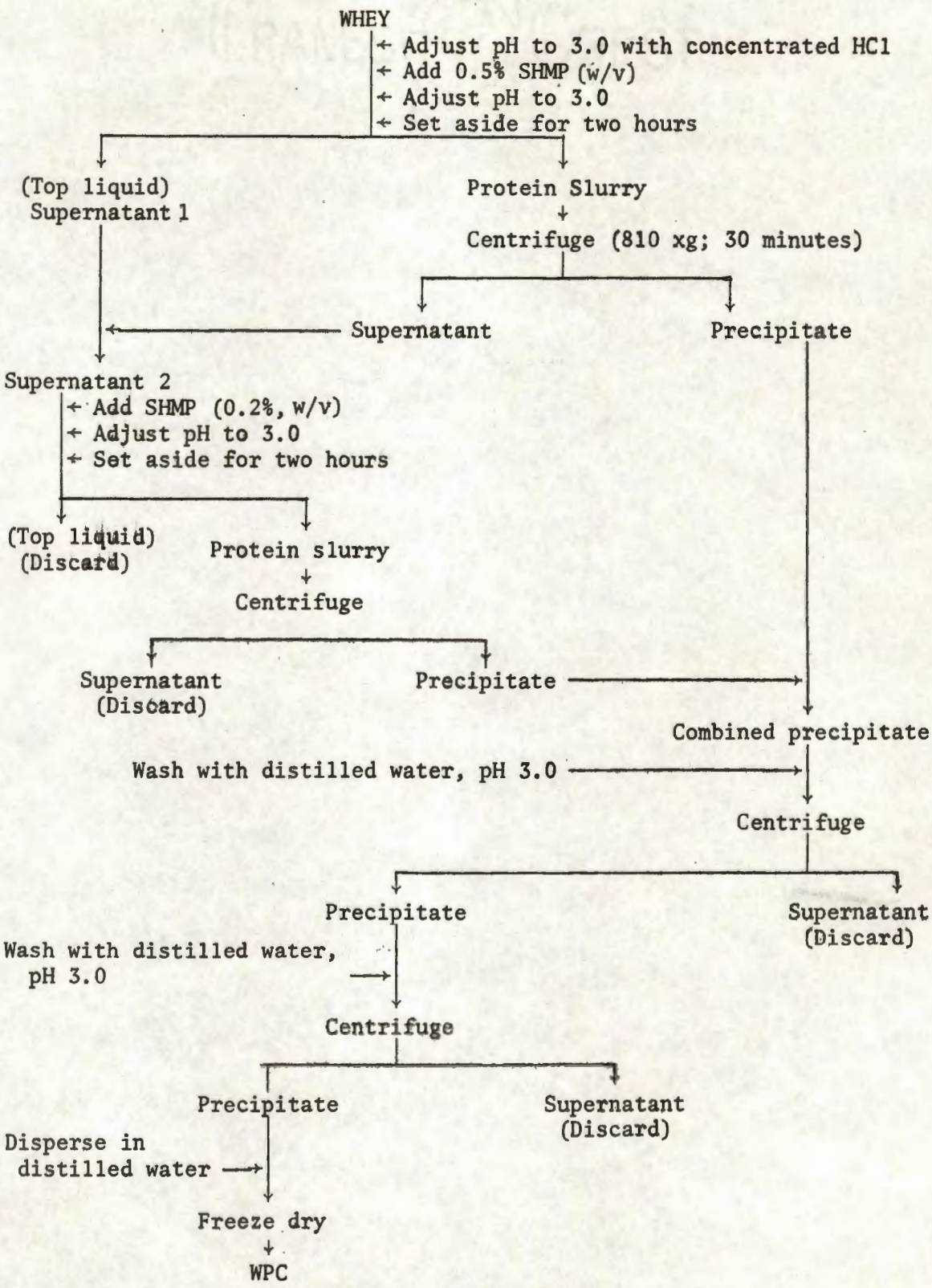


Figure 1. Preparation of whey protein concentrate.

concentration of 0.2 percent (w/v), and the pH was again adjusted to 3.0. The mixture was set aside for two hours. The top layer was removed as described and discarded.

The precipitates obtained from the whey and supernatant 2 were combined, washed twice with distilled water acidified to pH 3.0 and centrifuged. The final precipitate was dispersed in distilled water and freeze dried (sublimator, The Virtis Company, Gardiner, New York). The freeze dried WPC was ground and stored in glass bottles at room temperature until used.

WPC was analyzed for protein content by the Kjeldahl method (13), using a nitrogen conversion factor of 6.38. Moisture content was determined by drying in a vacuum oven at 58 ± 2°C for 24 hours. Ash was determined by the Association of Official Agricultural Chemists (A.O.A.C.) method for dairy products (13). The Babcock test for skimmilk (119) was employed to determine the fat content of a 5 percent WPC solution containing 2 ml of 0.2 N NaOH. Lactose was determined by the Chloramine-T method (85) using 10 ml of filtrate from a 5 percent WPC solution. The normality of Chloramine-T and $Na_2S_2O_3$ were 0.0419 and 0.0403, respectively. To calculate lactose concentration in WPC a correction of 1.1 ml/g protein was made for the volume of protein removed by filtration (90).

Phosphate in WPC was determined by a modification of the photometric amino reduction method suggested for determining phosphates in industrial waters by the American Society for Testing Materials (ASTM) (14). Absorbance (A) readings were taken at 830 nm as suggested by Meun and Smith (118) rather than 650 nm as suggested by ASTM. In the amino reduction

method for phoshorous, the reaction of orthophosphate with ammonium molybdate results in the formation of molybdophosphate. Molybdophosphate forms a molybdenum-blue complex with aminonaphtosulfonic acid. The color intensity is proportional to the phosphate concentration. Since only orthophosphate forms blue color, polyphosphates were converted to the reactive ortho form by boiling an acidified sample to cause hydrolysis (14).

Reagents:

Sulfuric acid, 37 percent.

Ammonium molybdate solution, 4.8 percent.

Amino solution: 3.7 g of anhydrous sodium sulfite (Fisher Scientific Co., Fairlawn, New Jersey), 0.10 g of 1-amino-2-naphtol-4-sulfonic acid (Fisher Scientific Co., Fairlawn, New Jersey) and 6.2 g of sodium metabisulfite (Mallinckrodt Chemical Works, St. Louis, Missouri) were dissolved in 100 ml of distilled water in the given order. The solution was stored in the dark and made up fresh every two weeks.

Standard phosphate solution: Indefinitely stable monopotassium phosphate (Fisher Scientific Co., Fairlawn, New Jersey) standard stock solution containing 80.0 micrograms of phosphorous per milliliters was prepared as described by Meun and Smith (118). Fresh working standards were prepared by suitable dilutions of the stock solution.

Procedure:

Two grams of WPC were dissolved in about 80 ml of distilled water. Two ml of 0.2 N NaOH were added, mixed and diluted to 100.0 ml with

distilled water. Duplicate samples of 0.1, 0.2, 0.3 and 0.4 ml were transferred into 100 ml volumetric flasks containing about 80 ml distilled water, mixed and diluted to volume. The sample was then transferred into a 250 ml Erlenmeyer flask, 5.0 ml sulfuric acid were added to each sample, mixed and boiled on a hot plate for at least 30 minutes. The volume was kept between 25 and 100 ml during boiling by adding distilled water.

Samples were cooled and diluted to 105 ml with distilled water. Five ml of ammonium molybdate solution was added into the solution and mixed. Five ml of amino solution was then added and the solution mixed again. The solution was set aside for nine minutes, and absorbance was measured with Spectronic 20 colorimeter equipped with a red filter and a red sensitive phototube (Bausch and Lomb Optical Co., Rochester, New York) at 830 nm. Readings were taken exactly between nine and eleven minutes against a water blank.

Respective absorbances of working standards containing 2, 4, 6, 8 and 10 micrograms of phosphorous per milliliter were determined by the same procedure. A standard phosphate regression equation in which phosphorous was expressed as orthophosphate was calculated.

Orthophosphate equivalents of samples were calculated from the regression equation $Y = - 0.0025 + 0.126\ X$ where Y and X are absorbance and micrograms orthophosphate per milliliter of solution, respectively.

Total phosphate was determined by using the equation:

$$\text{Total phosphate (mg/liter)} = C \times \frac{100}{S}$$

where

C = mg/l orthophosphate in sample calculated from values obtained with regression equation.

S = ml of sample used.

Total phosphate in WPC was calculated on weight percent basis and expressed as orthophosphate.

2. FIBER FORMATION BY WHEY PROTEIN CONCENTRATE

Three batches of WPC prepared by the procedure outlined in Figure 1 were used throughout the study. Fiber forming ability of WPC and the effect of various parameters on the production of single continuous fibers by the wet-spinning method were studied. All experiments were conducted at room temperature unless otherwise mentioned.

Fiber Forming Ability of Whey Protein Concentrate

Spinning Solution. A spinning solution was prepared by dissolving WPC in a solvent with constant stirring.

1. Spinning Solutions without Detergents:

The effects of WPC and NaOH concentrations on the fiber forming ability of WPC were studied with spinning solutions prepared with 0.1, 0.15, 0.20, 0.25, 0.50, 1.25 and 2.5 M NaOH as dispersing agent. WPC concentrations at each level of NaOH were 1 to 10 percent (w/v), in 1 percent increments, and 12.0 and 15 percent.

The effect of pH on fiber forming ability was determined by using 5, 10 and 15 percent aqueous WPC solutions. The pH was adjusted with 2.5 M NaOH from 7.0 to 12.0, in one unit increments.

The effect of reducing whey proteins in the pH range 7.0 to 12.0 on fiber formation was determined by adding 0.5, 1.0 and 2.0 percent β-mercaptoethanol (K & K Laboratories, Plainview, New York) to 10, 15 and 20 percent WPC solutions (w/v).

The ability of WPC to form fibers in the presence of casein (Nutritional Biochemicals Co., Cleveland, Ohio) was determined by adding casein to 8, 9, 10 and 12 percent WPC dispersions in 2.5 M NaOH. Spinning solutions were obtained either by (a) adding equal amounts of 4 or 10 percent casein solution (prepared with 2.5 M NaOH) to WPC dispersions; or (b) adding 1.5, 2, 4 and 5 times as much 12 percent WPC solution to a 10 percent casein solution.

2. Spinning Solutions with Detergents

Spinning solutions having 15, 20, 25 and 30 percent total solids were prepared by dispersing WPC in 20 percent aqueous solutions of Sodium lauryl sulfate (Fisher Scientific Co., Fairlawn, New Jersey), and Sodium dodecyl benzene sulfonate (K & K Laboratories, Plainview, New York). Three detergent to protein ratios, 0.5, 1.0 and 1.5, were employed at each level of total solids studied. Throughout this study, 0.5 percent β-mercaptoethanol was added to spinning solutions (v/v) and the pH was adjusted to 9.0, 10.0 or 11.0 with 50 percent (w/v) NaOH with constant stirring. At pH 9.0 spinning solutions of 20 and 25 percent total solids were further tested in the absence of β-mercaptoethanol and the presence of 0.5 and 2.0 percent β-mercaptoethanol.

Coagulating Bath. Table IV shows the variations in the composition of coagulating baths employed for determining the fiber forming ability of WPC, and for discussion purposes are designated one through ten.

Fiber forming ability of spinning solutions prepared in the absence of detergents was tested with an acid salt bath containing different concentrations of glacial acetic acid and sodium chloride.

The effect of coagulating bath pH on fiber formation was studied by raising the initial bath pH of 1.8 ± 0.1 to pH 4.5.

When spinning solutions containing detergents were tested, either coagulating bath 3 or bath 5 was used. Also hydrochloric acid-NaCl, sulfuric acid-NaCl and sulfuric acid-NaCl-formaldehyde baths were employed.

Variables pertaining to the effects of pH of the spinning solution, solvent and WPC concentration, incorporation of casein into WPC dispersions and reduction of whey proteins with β-mercaptoethanol were all studied with coagulating bath 3.

The coagulating bath was contained in a enamel pan (50 x 29 x 6 cm) and the solution was circulated in one direction, parallel to that of extrusion. The bath fluid was filtered through glass wool contained in glass tubing which in turn was connected to a 20 cm wooden pipe immersed in the bath. The inside diameter of the pipe was 1.0 cm. Along its length the pipe had six circular openings of 0.5 cm which were 2.0 cm apart. One end of the pipe was closed. Coagulating bath circulation was maintained by means of a rheostat attached to the pump.

TABLE IV

THE COMPOSITION OF COAGULATING BATH

Component	Coagulating Bath Designation									
	1	2	3	4	5	6	7	8	9	10
	percent									
Glacial acetic acid	7.5	10	12	15	12					
NaCl	7.5	10	12	15	12	5	5	5	5	5
HCl						5	10			
H_2SO_4								5	10	5
Formaldehyde					5					5
Distilled water	85	80	76	70	71	90	85	90	85	85
Total	100	100	100	100	100	100	100	100	100	100

Extrusion. Throughout the experimental period a variable speed Masterflex-Tubing Pump (Cole-Parmer Instrument Co., Chicago, Illinois) equipped with a 75 cm length of viton tubing (inside diameter, 0.08 cm) was employed for continuous extrusion of the spinning solution. The viton tubing was fitted to a 10 cm number 20 needle whose tip had been cut off. The tip of the needle was kept about 0.5 cm below the bath surface and about 5 cm in front of the wooden pipe to make certain that the spinning solution was extruded directly into the coagulating bath.

A simplified diagram of the spinning set-up used in determining the fiber forming ability of WPC is shown in Figure II.

Evaluation. For convenience, a six point evaluation scale was used in order (a) to differentiate among spinning solutions with respect to their fiber forming ability, and (b) to describe observed properties of resulting fibers according to the following scheme.

Evaluation scale designation	Properties of spinning solution and resulting fibers
-	Spinning solution dispersed in the coagulating bath.
+	Broken fibers were formed. Physical handling of fibers was not possible.
++	Continuous fiber was produced. Fiber was easily broken when it was slowly pulled away from the extrusion point, bent or stretched in the coagulating bath.

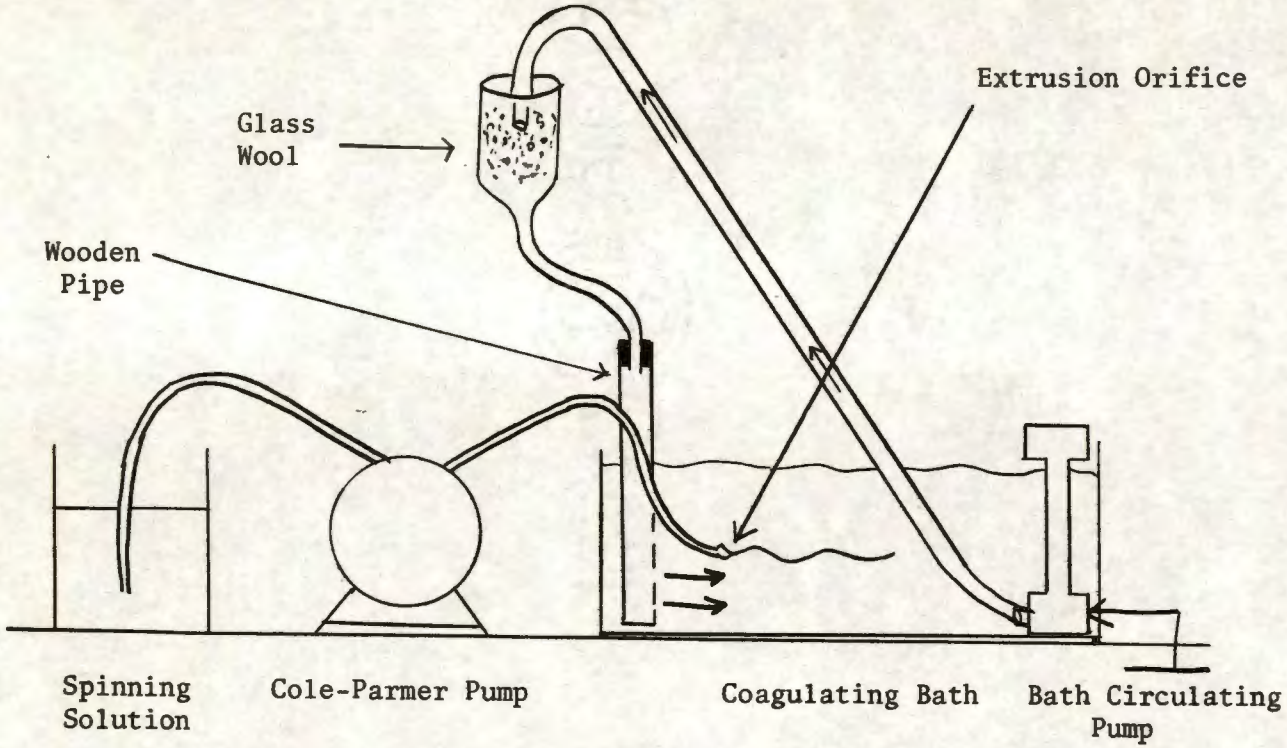


Figure 2. Simplified Diagram of Spinning Apparatus Used for Determining Fiber Forming Ability of WPC.

Evaluation scale designation	Properties of spinning solution and resulting fibers
++	Continuous fiber was produced. Fiber was easily broken when it was slowly pulled away from the extrusion point, bent or stretched in the coagulating bath.
+++	Continuous fiber could be physically turned in any direction in the coagulating bath. When the fiber was lifted to 10 or 15 cm above the bath surface, bent or stretched outside the coagulating bath, it was easily broken.
++++	Continuous fibers withstood physical handling as well as bending and stretching inside or outside the coagulating bath.
+++++	Production and handling of continuous fibers and the ability of fibers to be stretched was ideal.

Diffusion of Coagulating Bath into Spinning Solutions Prepared with Detergents and the Apparent Viscosity of Spinning Solutions

Diffusion. Diffusion of coagulating bath 3 (Table IV page 38) into the spinning solutions was observed under the following fixed conditions by the method outlined by Balmaceda and Rha (17).

Detergent	:	SLS and SDBS
Detergent/WPC	:	1.0 (w/w)
Detergent and WPC concentration	:	10, 12, 14 (w/v)
β-mercaptoethanol	:	0.5 percent (v/v)
pH	:	9.0
Time elapsed after preparation	:	0

The spinning solution was prepared by slowly adding precalculated amounts of WPC with β-mercaptoethanol to a detergent solution with constant stirring. The pH was adjusted in ten minutes with 50 percent (w/v) NaOH. Stirring was continued for 30 minutes and the solution was set aside for 15 minutes to deaerate. The end of the deaeration period was taken as zero time and the rate of diffusion was determined. Diffusion rate into 10, 12 and 14 percent WPC solutions at pH 9.0 was determined.

Two drops of spinning solution were placed on a microscope slide and another slide was applied to obtain a uniform layer of spinning solution between the two slides. This preparation was placed into a glass petri dish and covered with coagulating bath solution. The advancement of the boundary between coagulated and uncoagulated regions was microscopically measured at ten minutes intervals with an eye-piece micrometer.

Apparent viscosity. The effect of WPC and detergent concentration, type of detergent and time elapsed between the preparation of spinning

solution and extrusion on the apparent viscosity of the spinning solutions described in the diffusion studies was determined. The viscosity was determined at zero, six and twenty-four hours using 75 ml samples. A 13 cm glass cylinder having an inside diameter of 3.5 cm was used as the sample container. Viscosity was measured at room temperature with a Brookfield Synchro-Lectric LVT Model viscometer (Brookfield Engineering Laboratories, Staughton, Massachusetts) using cylindrical spindles. Measurements were taken two minutes after the spindle was immersed in the spinning solution. Readings were taken at 30-second intervals with the spindle and rpm which gave the highest reading. Readings were converted to centipoises using a factor finder chart supplied by the company and expressed as apparent viscosity.

Production of Continuous Fibers from WPC with Detergents

Spinning variables and equipment.

1. Spinning Solution

WPC-detergent spinning solutions were prepared as in the diffusion studies using 12 and 14 percent SDBS, 14 percent SLS and an equal amount of whey protein concentrate on a weight basis.

2. Coagulating Bath

A glacial acetic acid-NaCl solution (Table IV, bath 3, page 38) was used. The coagulating bath was circulated at a pumping rate of 400 ml per minute. The fiber residence time and the distance traveled by it in the coagulating bath were 5 to 15 seconds and 5 to 10 cm, respectively, during the stretching and collection of stretched fibers.

3. Extrusion

The equipment described for the study of fiber forming ability was employed. The maximum extrusion rates (as of zero time extrusion into the air) were 2.8 ml/minutes and 0.3 ml/minutes for spinning solutions prepared with 12 and 14 percent SDBS, respectively, and 0.5 ml/minutes for spinning solution prepared with 14 percent SLS.

4. Fiber Conveyor

An inclined fiber conveyor was used to transfer the fibers prepared with 12 percent SDBS from the coagulating bath to the take up reel.

An extended shaft of a Boudin speed reducing motor, type NSE-53R (Boudin Electric Co., Chicago, Illinois) equipped with a wooden spool (8 cm long, 1.5 cm inside diameter) was used to drive the conveyor. A second parallel shaft fitted to another spool the same size was fixed 4 cm above and 20 cm apart from the first shaft. A cloth belt passed around the two spools completed the system.

The conveyor was placed centrally on the immediate outside of the coagulating bath pan with a distance of 5 cm between the coagulating bath surface and the belt.

5. Take-Up Reel

A cross-shaped reel having its four arms (13 x 13 cm) perpendicular to one other was constructed from rigid plastic tubing 0.3 cm inside diameter. The axis of the reel was fitted to the extended shaft of a Boudin speed reducing motor, type NSE-11R (Boudin Electric Co., Chicago, Illinois). The motor with the reel attached to it was placed on a laboratory jack; thus the height of the reel from the coagulating bath

surface or from the conveyor was adjustable. The speed of the reel was regulated through a rheostat connected to the motor. The circumference of the reel was 75 cm.

The take up reel was placed 5 cm from the conveyor when the conveyor was in use and 10 cm from the edge of the coagulating bath when the conveyor was not used. In all conditions the height of the lower arm of the reel was fixed 20 cm above the coagulating bath surface. Throughout the study the take up reel was operated at a fiber collection speed of 1500 cm per minute.

The spinning set up described is sketched in Figure III with the conveyor and in Figure IV without the conveyor.

Collection of fibers. Fibers formed upon the extrusion of spinning solution into the coagulating bath were carried away from the extrusion point by the circulating coagulating bath. This resulted in the formation of a single continuous fiber. Three kinds of fibers were collected from each spinning solution at zero, six and twenty-four hours. For convenience the following descriptions were adopted to define and specify the types of fiber collected.

Unstretched fiber: The fiber picked up directly from the coagulating bath by hand at a length of 75 to 100 cm. In fact, the fiber defined here was stretched by (a) the motion of the coagulating bath, (b) the physical manipulation involved during the collection and (c) its own weight during the drying period.

Stretched fiber: When the traveling fiber was about to reach to the distal end of the coagulating bath it was transferred by hand either to

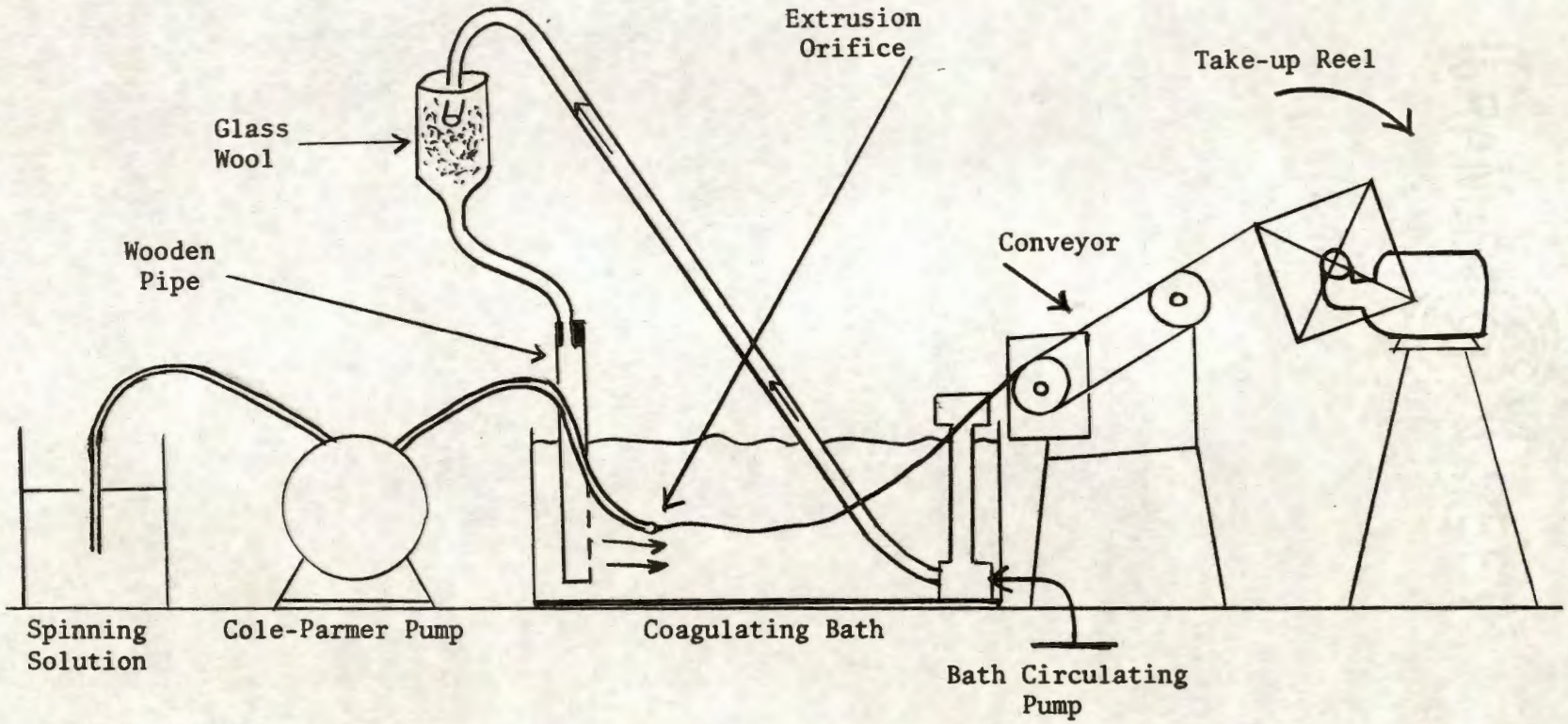


Figure 3. Fiber spinning apparatus with conveyor.

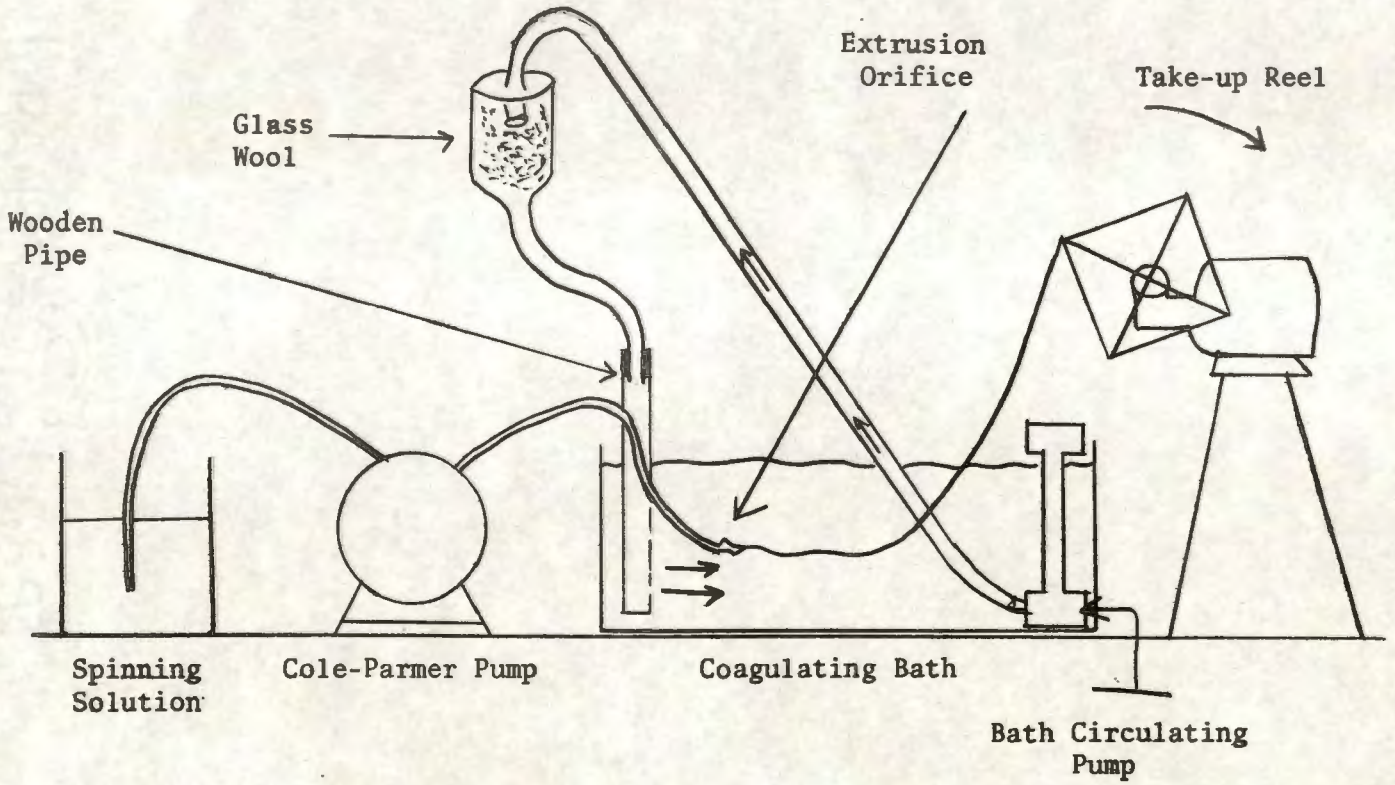


Figure 4. Fiber Spinning Apparatus without Conveyor.

the conveyor when it was used and from there to the take-up reel, or transferred directly to the take up reel when the conveyor was not used. The term, "stretched fiber", refers to fibers which were collected 75 to 100 cm in length by hand as it comes from the take-up reel.

Tow: A bundle of 100 stretched fibers obtained by continuous winding onto the reel.

Collected fibers and tows were dried at room temperature for 24 hours by hanging them on glass rods. Fibers then were cut into lengths of 25 to 30 cm and tows 10 to 12 cm.

Extraction of detergent from fibers. The method described by Lundgren (100,101,102,103,104) for removing detergents from egg-albumin fibers was utilized. Dried fibers and tows obtained from each spinning solution at each time level were divided into two sets. One set was treated with 60 percent aqueous acetone and the other with 60 percent aqueous acetone containing 5 percent potassium chloride.

Five hundred milliliters of extracting medium were put in a pyrex dish (26 x 16 x 4 cm). Fibers and tows were immersed in the medium, the dish was covered with parafilm, and the cover was secured with a rubber band.

Fibers were treated for 24 hours and tows for 48 hours. At the end of the extraction period, they were transferred into distilled water and allowed to rinse for 15 to 20 minutes. Then the fibers and tows were dried at room temperature on glass rods for 30 minutes and the resulting products were termed "finished fibers" and "tows". These were stored at room temperature for future use.

Finished fibers and tows were analyzed for protein, residual detergent and phosphate content. Fiber diameter, tensile strength and elongation of fibers were determined.

Diameter, tensile strength and elongation of finished fibers. Fibers and tows were conditioned to 70 percent relative humidity at 25°C for at least 48 hours before measurements were taken. Fiber diameter was determined microscopically with an eye-piece micrometer. A fiber piece of 4 to 5 cm was used for measuring the diameter and ten measurements were taken on each fiber sample. The remaining portion of the fiber, after the sample for diameter measurement was taken, was cut into two pieces and both pieces were tested on an Instron Universal Testing Machine, model 1782, equipped with a potensiometric type graphic recorder (Instron Corporation, Canton, Massachusetts). Operating conditions of the Instron were set as follows:

Tension load cells used	:	Cell A for fibers and cell B for tows.
Full scale load used	:	10 g for fibers and 100 g for tows.
Gage length used	:	5.08 cm.
Crosshead speed used	:	25.4 cm/minute.
Chart speed used	:	25.4 cm/minute.
Elongation	:	20 percent/cm chart travel.

Tensile strength and elongation were calculated from the stress-strain curves obtained.

Analysis of finished fibers and tows. Finished fibers and tows were dried in a vacuum oven for 24 hours at 58 ± 2°C. Duplicate samples of

50 to 100 mg were accurately weighed into 10 ml volumetric flasks. Five milliliters of 0.85 percent NaCl were added and the flask gently swirled until all the sample was wetted. Samples were then diluted to volume with 0.2 N NaOH and set aside for 2 hours with occasional swirling. This solution was designated as the sample stock solution and protein, phosphate and detergent were determined as described below:

1. Protein: A modification of the Biuret Method suggested for determining total protein in serum by the Interdepartmental Committee on Nutrition for National Defense (89) was used. Duplicate samples of 0.5 ml each were transferred from the sample stock solution into test tubes containing 2.5 ml of 0.85 percent NaCl and mixed. Three milliliters of Biuret reagent was added and the contents mixed again. After standing for at least 30 minutes the samples were transferred into curvettes and the absorbance was read at 540 nm on a Spectronic 20 calorimeter. Readings were corrected for a blank containing 0.25 ml of 0.2 N NaOH, 2.75 ml of 0.85 percent NaCl and 3.0 ml of Biuret reagent.

The protein content of WPC was determined by the Kjeldahl method and was used as the standard protein in determining the protein regression equation for fibers. The protein content of fibers and tows were calculated from the regression equation $Y = - 0.00592 + 0.06116 X$ where Y and X are the absorbance and total protein in the sample tested, respectively. Protein content of fibers and tows were expressed on a weight percent basis.

2. Phosphate: One millileter of the stock sample solution was transferred into a 100 ml volumetric flask containing about 80 ml

distilled water, mixed well and diluted to volume with distilled water, and transferred into a 250 ml Erlenmeyer flask. The phosphate content was determined as described for phosphate in WPC.

3. Detergent: The method described by Wisherchen (175) for quantitative determination of SLS in powdered egg-white was modified for determining residual SLS and SDBS in finished fibers and tows. In the original method the sample was dissolved in water and the protein was precipitaed with ethyl alcohol and filtered off. The filtrate was evaporated and was dissolved in water and adjusted to pH 5.0. Total alkyl sulfates were titrated with standard benzethonium chloride solution in the presence of chloroform with bromphenol blue indicator. The formation of bromphenol blue-benzethonium chloride complex when excess benzethonium chloride was present was taken as the end point (175).

Reagents: The reagents used were prepared according to the procedure given by Wisherchen (175). The amount of reagents used for the test were reduced by a factor of five. The normality of acetous perchloric acid was 0.073; purity of benzethonium chloride was 81.6 percent and the normality of benzethonium chloride solution was 0.00164. The detergent equivalent of 1.0 ml benzethonium chloride solution was 0.571 mg of SDBS and 0.473 mg of SLS.

Procedure: The remaining 8.0 ml sample stock solution was transferred into a 50 ml Erlenmeyer flask and 40 ml ethyl alcohol was added and the flask gently swirled for a minute. The mixture was then heated on a steam bath for 30 minutes and cooled for 30 to 45 minutes. Then it was centrifuged at 410 xg for 20 minutes. The supernatant was

poured into a 50 ml beaker and evaporated to dryness on a steam bath while passing a current of air above the surface of the liquid. The residue was dissolved in 25 ml distilled water, set aside for 10 minutes and the pH was adjusted to 5.0 ± 0.1 N HCl and 0.5 N NaOH.

The resulting solution was transferred into a 50 ml Erlenmeyer flask. Ten milliliters of chloroform and 0.1 ml bromphenol blue indicator were added along with 50 mg of anhydrous sodium sulfate. The mixture was then titrated with benzethonium chloride solution to the blue-green end point. Benzethonium chloride was added in small proportions and the mixture was vigorously stirred for 10 seconds after each addition and the layers were allowed to separate for 30 seconds before the next addition.

The volume of benzethonium chloride spent was corrected for a blank titration performed along with the sample. The amount of detergent expressed as percent of sample weight was calculated from the following equation:

$$\text{Detergent (\%)} = \frac{\left[\begin{array}{c}\text{ml of 0.00164 N benzethonium} \\ \text{chloride used}\end{array}\right]\left[\begin{array}{c}\text{mg detergent equivalent of} \\ \text{one ml benzethonium chloride}\end{array}\right]}{\text{mg of sample stock solution tested}} \times 100$$

3. SOME PROPERTIES OF FIBERS PREPARED WITH WPC AND DETERGENTS

Behavior in Water before Detergent Extraction

Fibers and tows immediately after production (wet-state) and/or after drying at room temperature (dry-state) were placed in glass petri dishes containing distilled water. Visible physical events taking place were followed for ten minutes and recorded.

Resistance of Finished Fibers to Boiling in Water and Water Absorbtion

Resistance to boiling in water. Five samples of finished fibers, each approximately two grams, were immersed in about one liter of boiling distilled water and boiling continued for 30 minutes. Observations were recorded.

Water absorbtion. Ten samples of finished fibers, each approximately one gram, were immersed in boiling distilled water for 10 minutes. The samples were then blotted on filter paper (Whatman #1) for exactly one minute and weighed. Fibers were weighed again after drying in a vacuum oven at 58 ± 2°C for 24 hours. Absorbed water was determined as the difference in two weights and expressed as percent weight of dry finished fibers.

4. STATISTICAL METHODS

The Statistical Analysis System (18) Computer Program at the University of Tennessee Computer Center (UTCC) was used for the calculation of Analysis of Variance. Data concerned with apparent viscosity of spinning solutions, composition and physical properties of finished fibers were analysed as a Split Plot Design. Effect of fiber diameter on tensile strength and elongation was determined by regression analysis using the diameter as a continuous variable. Difference between means were analyzed by Tukey's W-procedure (156) for factors indicated as significant by analysis of variance.

CHAPTER IV

RESULTS AND DISCUSSION

1. WHEY PROTEIN CONCENTRATE

The composition of WPC used in fiber studies and prepared by the process outlined in Figure I is shown in Table V. The mean protein content of cottage cheese whey was 0.88 percent. The resulting WPC had a protein content comparable to those reported in the literature for various processes (Table I page 6). The advantage of the process followed in this study reflected in the low lactose content of WPC and was apparently due to repeated washings included in the process.

Total protein recovery from whey was low (59.53 percent). Reference was made in the literature review to the effect of mineral composition of whey on protein recovery by the SHMP-complexing method (83). Reported high protein recoveries (76,83) include a decationization step in the preparation of WPC by this method.

Concentration of components indicated in Table V does not add up to one hundred percent. WPC has been reported to contain 0.45 to 0.52 g of bound water per gram of protein (22). Thus, Table V suggests the presence of some bound water in WPC.

2. FIBER FORMING ABILITY OF WHEY PROTEIN CONCENTRATE

The effect of variations in the pH and composition of the acetic acid-NaCl coagulating bath (Table IV page 38) on the quality of fiber

TABLE V

COMPOSITION OF WHEY PROTEIN CONCENTRATE EMPLOYED IN FIBER STUDIES

Component		Percent[a]
Protein (N x 6.38)		70.78
Lactose		2.67
Fat		3.06
Total $PO_4^{\equiv}$	4.28	
Ash		11.40
Moisture		4.57
Total		92.48

[a]Means of three batches analyzed with four replicates.

obtained throughout the experimental period was not detectable by observation. Studies with bath 3 consistently resulted in reproducible observations. Therefore, bath 3 was used in all experiments concerned with fiber forming ability of WPC.

Spinning Solutions Without Detergents

The literature shows no evidence that aqueous alkaline WPC dispersions have been studied with respect to their fiber forming ability. However, on a commercial scale 5 to 20 percent NaOH and 15 to 30 percent protein material has been successfully used to prepare spinning solution of various other proteins in the pH range between 8.5 and 13.5 (Table II page 18). In previous studies concerned with the preparation of protein fibers on a laboratory scale the maximum amount of proteinaceous material incorporated into spinning solutions ranged from 16.5 percent for zein (protein content of zein was not specified) (44) to 25 percent for single cell protein (SCP) (protein content of SCP was 51 percent) (87). The concentration of NaOH used during the preparation of spinning solutions was found to determine the limits of protein concentration in the spinning solution (95).

Boyer (26,28) observed difficulties in the preparation of soy protein dispersions having more than 12 percent solids because of the tendency of proteins to form gels in high concentrations. In addition to gel formation, Huang and Rha (87) experienced physical difficulties in the preparation and handling of spinning solutions containing high concentrations of single cell protein. In practice, all these difficulties were overcome by aging spinning solutions at certain temperatures (25 to 45°C) for certain periods of time (1 to 7 days) (44,87,104).

Results of the present study on the effects of WPC and NaOH concentrations, pH, β-mercaptoethanol and casein on fiber forming ability of WPC and the observed properties of resulting fibers are summarized in Tables VI through IX. Comprehensive evaluation of the results in Table VI suggests several things. Four percent or higher concentrations of WPC in the spinning solution were required for fiber formation. Seven and 9 percent WPC dispersions, prepared with 0.25 and 0.20 M NaOH respectively, appeared to provide minimum conditions for continuous fiber formation. Gel formation appeared to limit the use of higher concentrations of WPC (15 percent) and NaOH (0.25 M and above). Preparation of spinning solution with increased concentration of WPC and/or NaOH did not affect the quality of continuous fibers to a marked degree. Adjusting the pH of spinning solutions between 7.0 and 12.0 (Table VII) did not seem to affect fiber forming ability at the low WPC concentration (5 percent). Increased WPC content (15 percent) appeared to lower the pH at which continuous fiber formation first occurred. However, raising the pH did not improve the quality of continuous fibers beyond the ++ judgement level.

Addition of β-mercaptoethanol to spinning solutions expanded the pH range for continuous fiber formation for 10 percent WPC dispersions (Table VIII). Three levels of β-mercaptoethanol used(0.5, 1.0 and 2.0 percent) did not cause visible differences in the quality of continuous fibers obtained from 10 percent WPC dispersions. Handling properties of continuous fibers obtained from 15 percent WPC solutions were improved equally by 0.5 and 1.0 percent β-mercaptoethanol. Furthermore, continuous

TABLE VII

EFFECT OF pH ON FIBER FORMATION OF WPC DISPERSIONS AT VARIOUS WPC CONCENTRATIONS

WPC Concentration (%)	pH[a,b]					
	7	8	9	10	11	12
5	+	+	+	+	+	+
10	+	+	+	+	++	++
15	+	+	++	++	++	++

[a]Adjusted with 2.5 M NaOH.

[b]Three observations.

TABLE VIII

EFFECT OF β-MERCAPTOETHANOL ON FIBER FORMATION BY WPC AT VARIOUS pH LEVELS

	WPC Concentration (%)[a]								
	10			15			20		
	Mercaptoethanol Added (% v/v)								
pH	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
7	+	+	+	+	++	+	+	+	+
8	+	+	+	+	++	+	+	+	+
9	++	++	++	+++	+++	+++	+++	Gel	Gel
10	++	++	++	+++	+++	+++	Gel	Gel	Gel
11	++	++	++	+++	+++	Gel	Gel	Gel	Gel
12	++	++	++	+++	+++	Gel	Gel	Gel	Gel

[a]Three observations.

TABLE IX

FIBER FORMING ABILITY OF WPC-CASEIN MIXTURES IN 0.25 M NaOH

Spinning Solution Mixture				
Total Solids (%)	WPC (%)	Casein (%)	WPC/Casein	Fiber Formation[a]
6.5	4.5	2.0	2.25	+++++
7.0	5.0	2.0	2.50	+++++
8.0	6.0	2.0	3.00	+++++
9.0	4.0	5.0	0.80	+++++
9.5	4.5	5.0	0.90	+++++
10.0	5.0	5.0	1.00	+++++
11.0	6.0	5.0	1.20	+++++
11.33	8.0	3.33	2.40	+++
11.60	9.6	2.0	4.80	+++
11.66	10.0	1.66	6.02	+++

[a]Three observations.

fiber formation occured over the entire pH range studied (pH 7.0 to 12.0). Gel formation resulted when 2.0 percent β-mercaptoethanol was added to 15 percent WPC dispersion above pH 10.0. The three levels of β-mercaptoethanol added to 20 percent WPC dispersion resulted in gelation in all cases at pH 10.0 or higher. All the spinning solutions forming continous fibers at pH 9.0 and above gelled within 30 to 45 minutes after their preparation.

WPC-casein mixtures (Table IX page 61) ranging in total solids content from 6.5 to 11.0 percent and having a WPC to casein ratio of 0.8 to 3.0 formed continuous fibers with excellent handling properties. However, as little as 0.33 percent increase in total solids over 11.0 percent resulted in the reduction of fiber quality when the WPC to casein ratio was 2.4.

In conclusion, the present study did not give specific information by which the requirements for continuous fiber formation by WPC could be met. The study indicated, however, that spun protein fibers can be produced from aqueous alkaline WPC dispersions, the reduction of whey proteins with β-mercaptoethanol has a positive effect on fiber forming ability of WPC and on the quality of resulting fibers, and the presence of small amounts of the fiber forming protein, casein, in whey may not affect the fiber forming ability of WPC.

Spinning Solutions with Detergents

Studies concerned with the effects of pH, total solids, detergent to WPC ratio and β-mercaptoethanol on the fiber forming ability of spinning

solutions prepared with WPC and detergents and the quality of fibers produced are summarized in Tables X and XI. Observations indicated that WPC-detergent spinning solutions prepared with both detergents, sodium lauryl sulfate and sodium dodecyl benzene sulfonate, behaved similarly under all experimental conditions and formed continuous fibers whenever spinning was possible. In the absence of β-mercaptoethanol at pH 9.0 (Table X) the quality of fibers obtained was not markedly improved over those fibers obtained from WPC-NaOH (Table VI page 58) or WPC-NaOH-Mercaptoethanol (Table VIII page 60) dispersions. The addition of β-mercaptoethanol to WPC-detergent spinning solutions definitely improved the handling properties of fibers (Table X) at the 0.5 percent level. Two percent β-mercaptoethanol together with low detergent to WPC ratio (0.5, Table X) and/or high total solids and high pH (30 percent total solids and pH 10.0 and 11.0, Table XI) resulted in gel formation. Spinning solutions having the low detergent to WPC ratio (0.5) appeared to produce lower quality fibers than those spinning solutions with high detergent to WPC ratios (1.0 and 1.5, Tables X and XI). At high detergent to WPC ratios, fiber quality improved with increased total solids in the spinning solution up to 25 percent total solids. The effects of pH here on handling properties of fibers was not detectable by observation. A detergent to WPC ratio of 1.0 or 1.5 resulted in easy preparation, physical handling and extrusion of spinning solution.

The fiber forming property that appears when proteins were treated with certain anionic detergents were investigated first by Lundgren (104). He observed that egg albumin-SDBS spinning solutions having detergent to

TABLE X

FIBER FORMING ABILITY OF WPC-DETERGENT SOLUTIONS[a] AT pH 9.0 IN THE PRESENCE AND ABSENCE OF β-MERCAPTOETHANOL

Total Solids (%)	Detergent/WPC	β-Mercaptoethanol Concentration[b] (%)		
		0	0.5	2.0
20	0.5	++	++	Gel
	1.0	++	+++	+++
	1.5	++	++++	+++
25	0.5	++	+++	Gel
	1.0	+++	+++++	++++
	1.5	+++	+++++	++++

[a]SDBS or SLS.

[b]Three observations.

TABLE XI

FIBER FORMING ABILITY OF WPC-DETERGENT[a] SOLUTIONS CONTAINING 0.5 PERCENT β-MERCAPTOETHANOL AT VARIOUS TOTAL SOLIDS CONTENT, DETERGENT/WPC RATIO AND pH LEVELS

Spinning Solution		pH[b]		
Total Solids (%)	Detergent/WPC	9	10	11
15	0.5	++	++	++
	1.0	+++	+++	+++
	1.5	+++	+++	+++
20	0.5	++	++	++
	1.0	++++	++++	++++
	1.5	++++	++++	++++
25	0.5	+++	+++	+++
	1.0	+++++	+++++	+++++
	1.5	+++++	+++++	+++++
30	0.5	++	Gel	Gel
	1.0	+++	+++	+++
	1.5	++++	++++	++++

[a]SDBS or SLS.

[b]Three observations.

egg albumin ratios of 0.66 to 1.5 and 18 to 24 percent total solids provided optimum conditions for spinning. Best results were obtained with a slight excess of detergent in the presence of 0.1 percent mercaptoethanol (102,104). Aged spinning solutions proved better for spinning than those freshly prepared.

In agreement with Lundgren's findings, best results were obtained in the present study with WPC-detergent spinning solutions containing 25 percent total solids and detergent to WPC ratios of 1.0 and 1.5 in the presence of 0.5 percent β-mercaptoethanol (Table XI page 65). Detergent induced solubilization of proteins (77,102) might have caused the differences observed in handling properties of fibers obtained from WPC-detergent solutions having low (0.5) and high (1.0 to 1.5) detergent to WPC ratios (Table XI page 65). The ability of reduced proteins to bind more detergent than their native counterparts (88,138), together with detergent induced solubility, might have some bearing on the differences observed in handling properties of fibers made from WPC-detergent, WPC-detergent-mercaptoethanol dispersions (Table X page 64), WPC-NaOH-mercaptoethanol and WPC-detergent-mercaptoethanol dispersions (Tables VIII and XI, pages 60 and 65, respectively). This explanation is self limiting by the presumably complicated nature of protein-detergent interactions, the number of parameters tested, and the nature of the evaluation method used. Nevertheless, the study indicated that continuous spun protein fibers can be prepared from WPC-detergent mixtures. In the presence of 0.5 percent β-mercaptoethanol the handling properties of fibers were significantly improved with increased total solids and

detergent to WPC ratio. At pH values above 9.0 there was no additional beneficial effect on observed fiber properties. Therefore, pH 9.0 was chosen for all further work.

3. DIFFUSION OF COAGULATING BATH INTO SPINNING SOLUTION

Diffusion of the coagulating bath into spinning solutions was determined to relate it to pertinent spinning variables in future studies such as the relationship between fiber residence time in the coagulating bath and strength of resulting fibers, and to obtain information on the differences observed in handling properties of fibers made with aqueous alkaline WPC dispersions and WPC-detergent solutions at pH 9.0.

Table XVIII in the Appendix shows the rate of the movement of the coagulation boundary with time for WPC, WPC-SDBS and WPC-SLS spinning solutions containing 10, 12 and 14 percent WPC. The advancement of the coagulation boundary was plotted against time in Figure V for spinning solutions of 14 percent WPC, WPC-SDBS and WPC-SLS. The data indicates that the advancement of the boundary was rapid at the beginning then gradually declined for all spinning solutions tested. WPC dispersion alone coagulated faster than WPC-SDBS and WPC-SLS dispersions (Figure V).

Assuming a diffusion limited chemical reaction Balmaceda and Rha (17) studied the coagulation of 29.4 and 38.4 percent zein dispersions in aquous HCl solutions at pH 3.0 and 32, 75, 96 and 116°F. They found that the diffusion of coagulating bath into zein dispersions increased with temperature up to 96°F then suddenly decreased. Length of the coagulated layer in the first ten minutes was about 0.06 and 0.07 cm

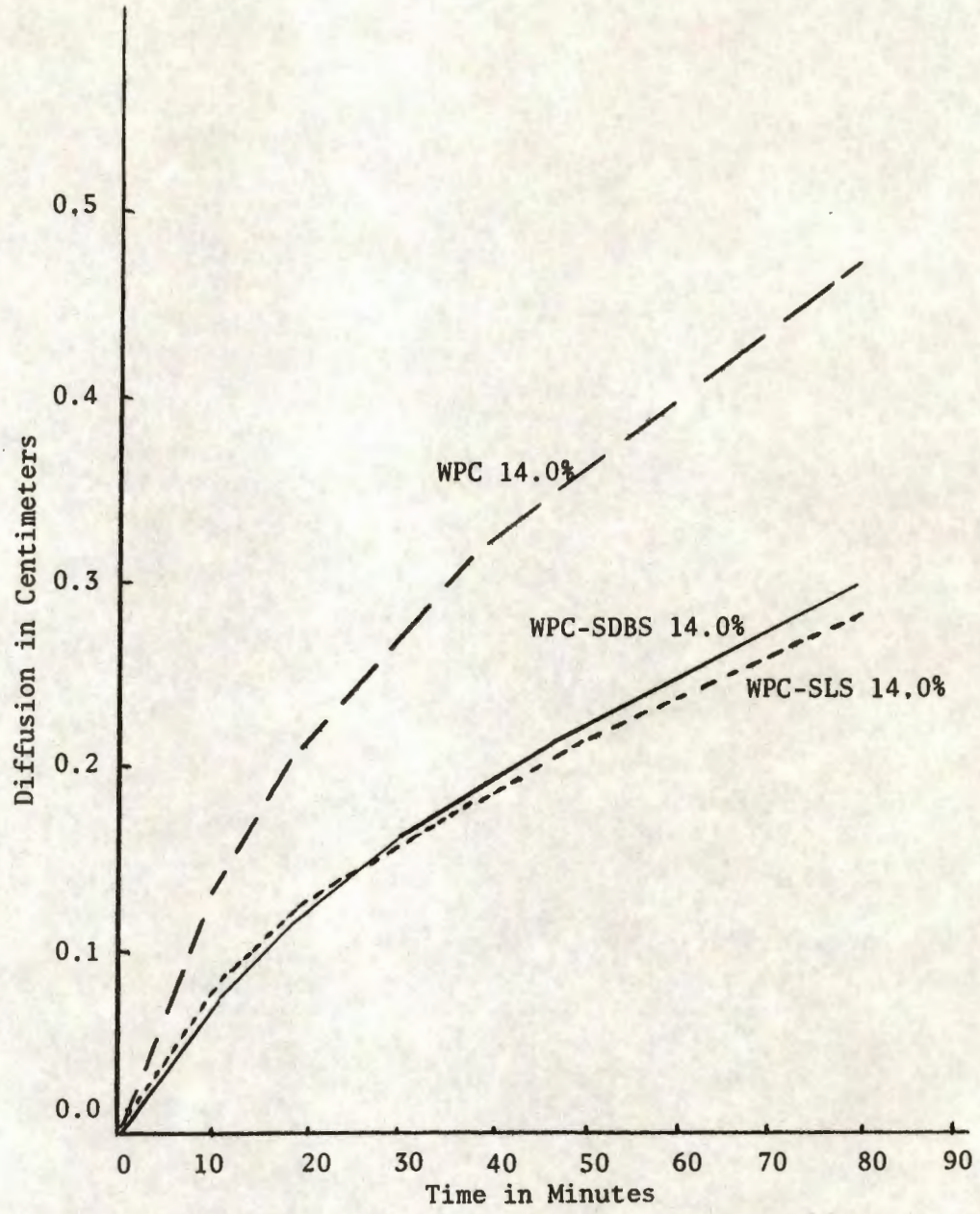


Figure 5. Diffusion of coagulating bath into spinning solution.

for 38.4 and 29.4 percent zein dispersions respectively. Although their study includes an additional important parameter, temperature, the particular temperature used was not stipulated for their plot of diffusion versus time. Figure V (page 68) suggests that diffusion of coagulating bath into 14 percent WPC-detergent solutions in the first ten minutes (0.068 cm for WPC-SDBS spinning solution and 0.078 cm for WPC-SLS solution, Table XVIII in the Appendix) were close to the diffusion values reported for zein dispersions.

4. APPARENT VISCOSITY OF SPINNING SOLUTIONS PREPARED WITH WPC AND DETERGENTS

Apparent viscosity for various time intervals for spinning solutions containing 0.5 percent β-mercaptoethanol and prepared with 10, 12 and 14 percent WPC and detergents at pH 9.0 is tabulated in Table XIX in the Appendix. Apparent viscosity of spinning solutions was determined in order to obtain fundamental information concerned with selection and description of spinning conditions and spinning solutions for continuous fiber production, and to find relationships between the viscosity of spinning solutions and properties of spun WPC fibers.

Viscosities of WPC-detergent spinning solutions at zero time (Figure VI) were higher than corresponding viscosities of WPC and detergent solutions alone. Apparent viscosities at zero time for 10, 12 and 14 percent WPC dispersions were 4, 4.8 and 5.5 centipoise. SDBS dispersions had apparent viscosities of 2.5, 2.9 and 3.4 centipoise and SLS dispersions had viscosities of 3.0, 3.5 and 3.9 centipoise. Figure VI

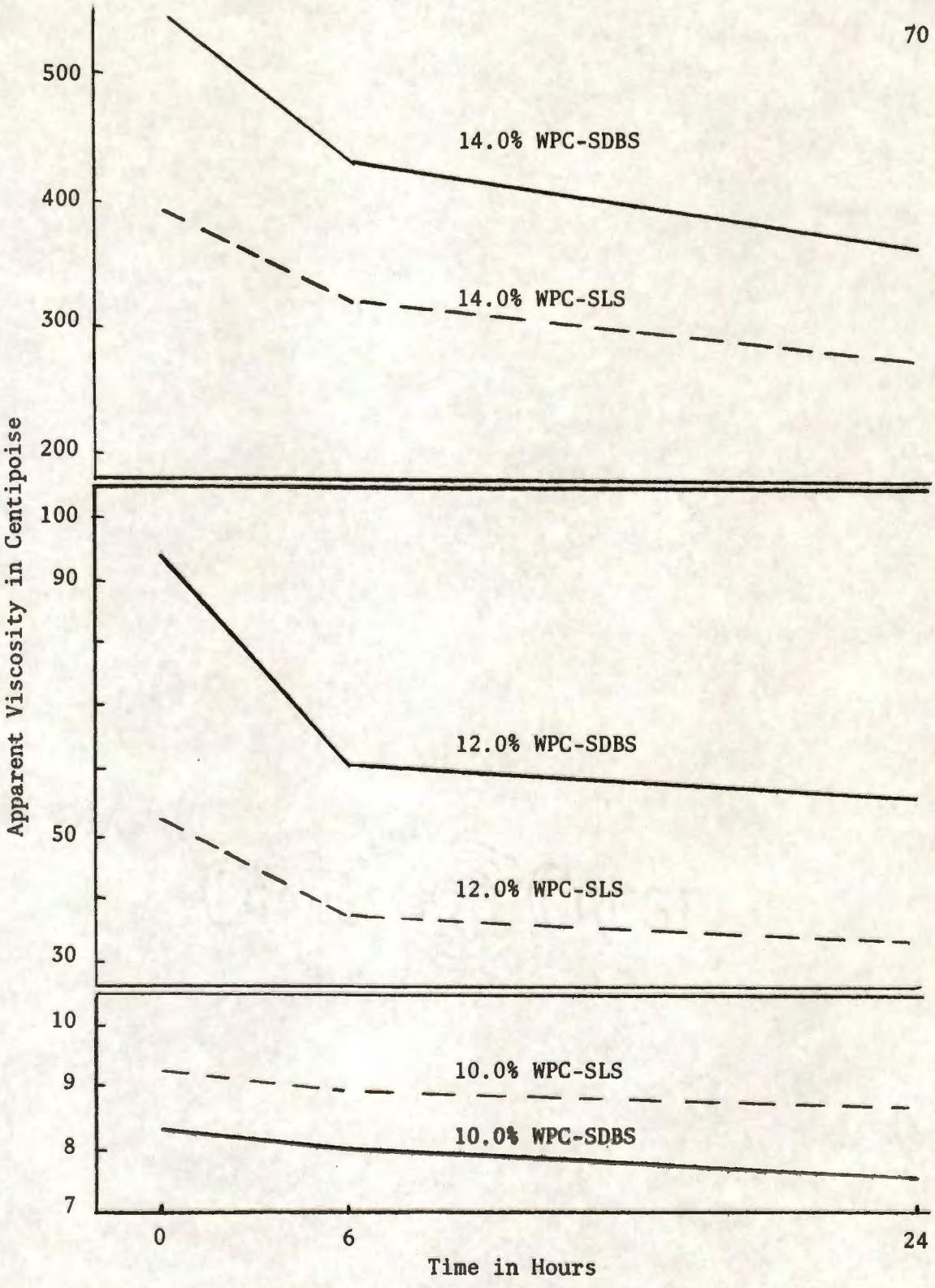


Figure 6. Change in apparent viscosity with time for spinning solutions prepared with WPC and detergents.

shows that the apparent viscosity of spinning solutions prepared with WPC and detergents increased with increased WPC and detergent concentration and decreased with time. In agreement with Figure VI, analysis of variance (Table XX, Appendix) indicated that the concentration of WPC and detergent used, time elapsed before spinning and their interaction had significant effects on the apparent viscosities of spinning solutions ($P < 0.001$). Analysis of variance did not reveal any difference in the apparent viscosity due to detergent type used. As suggested by Figure VI, comparison of means showed, however, that apparent viscosity of spinning solutions prepared with both detergents at 10 and 12 percent levels had a similarity in decrease with time within each concentration level (Table XIX, Appendix). In addition, the viscosity of 14 percent WPC-detergent solutions was significantly influenced ($P < 0.05$) by the type of detergent used.

5. PROPERTIES OF FIBERS PREPARED WITH WPC AND DETERGENTS

Similarity in fiber forming ability of spinning solutions prepared with both detergents and similarity in handling properties of resulting fibers have been mentioned already. Photographs of all three types of fibers prepared with WPC and SDBS taken before detergent extraction are presented in Figures VII and VIII. Regardless of their type (stretched, unstretched or tow) and condition (wet or dry state), all fibers before the extraction of detergent completely and quickly disintegrated when they were brought into contact with water. However, wet fibers immersed into water at the immediate end of the detergent extraction period, or

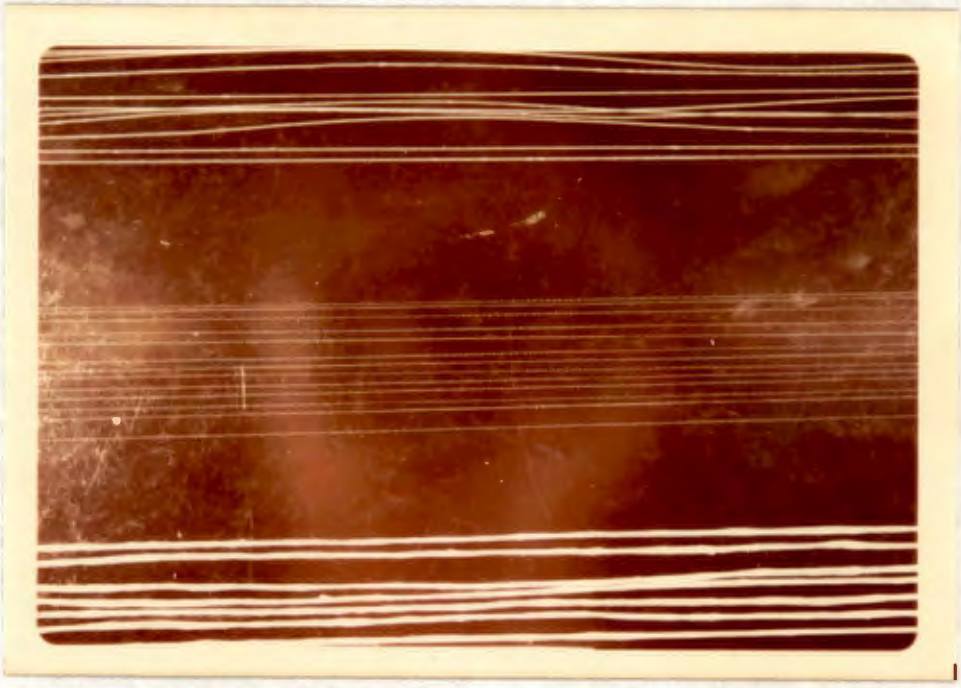


Figure 7. WPC-SDBS fibers (at the top: unstretched fibers, in the middle: stretched fibers) and tows (at the bottom) before detergent extraction.



Figure 8. WPC-SDBS stretched fibers before detergent extraction.

finished fibers (extracted and dried) boiled for 30 minutes in water retained their integrity. Water absorbed by finished fibers ranged between 1.04 and 1.34 times the dry weight with an average of 1.23 fold water absorbtion. Upon boiling in water finished fibers became flexible, stretchable and pliable. These observations indicate that whey proteins were in their native state in the fibers prior to detergent extraction and denatured with extraction. Therefore stretched finished fibers should preserve their fibrous form in food applications involving water.

The photograph in Figure IX shows a view of a tow during its preparation on the take-up reel. Stretched fibers adhered to each other during winding of fibers into tows. Furthermore, separation of indivdual fibers from the tows did not occur in any experiments concerned with water absorbtion and resistance of finished fibers to boiling in water. These facts suggest that whey protein fibers may not require the presence of a binder in food applications. However, comparing the appearence of fibers before the extraction of detergent (Figures VII and VIII) and finished fibers (Figure X), the latter showed a spiral or curled appearance. The photomicrographs shown in Figures XI and XII did not have sufficient magnifications to provide structural information. Factors contributing to the differences in the appearence of fibers before and after detergent extraction may include drying of fibers without tension after the extraction of detergent and cavities created in the fiber structure by the outgoing detergent. Lundgren (101,104) suggested that fibers could be subjected to steam and a stretching operation after the extraction of detergent.

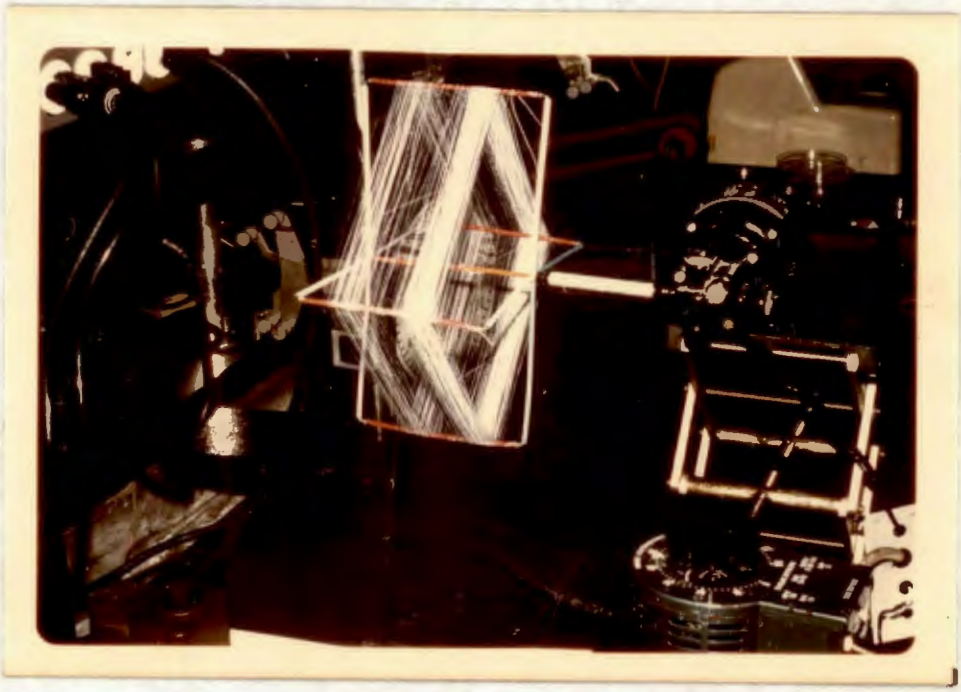


Figure 9. WPC-SDBS tow on take-up reel at the time of its preparation.

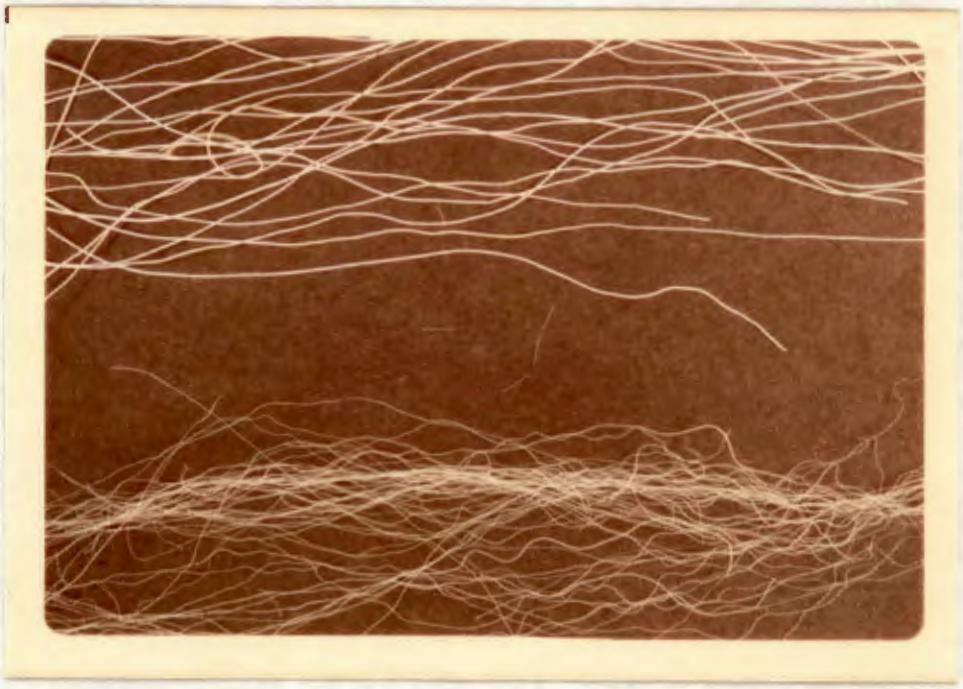


Figure 10. Unstretched (at the top) and stretched (at the bottom) WPC-SDBS fibers after detergent extraction.



Figure 11. Photomicrograph of stretched WPC-SDBS fibers after detergent extraction (magnification: 40x).



Figure 12. Photomicrograph of detergent extracted-stretched WPC-SDBS fiber (magnification: 400x).

Tables XII, XIII and XIV show the diameter, tensile strength and elongation at break for stretched and unstretched finished fibers prepared with WPC and SDBS. Data indicated that stretched fibers had smaller diameter than unstretched fibers (Table XII). The influence of fiber type on diameter was statistically significant at the 0.01 level of probability (Table XXI, Appendix). Fiber diameter was affected also by the interaction between time and WPC and detergent concentration ($P < 0.001$) and by the interaction among time, fiber type and WPC and detergent concentration ($P < 0.05$). Analysis of variance indicated that fiber diameter was not significantly affected by WPC and detergent concentration used and time elapsed before spinning (Table XXI, Appendix). When means were compared however (Table XII) diameter of fibers prepared with 14 percent WPC and SDBS appeared to be significantly smaller than the diameter of fibers prepared with 12 percent WPC and SDBS ($P < 0.05$). Variation in the diameter of fibers prepared at various time intervals was also significant at 0.05 level of probability (Table XXI, Appendix).

Tensile strength of WPC-SDBS fibers was significantly higher at the 0.05 level of probability than the tensile strength of unstretched fibers (Tables XII and XXI). This was the only significant effect. Regression analysis of the data showed that the tensile strength increased as the diameter decreased according to the following equation:

$$\text{Tensile strength} = 23269.18 - 57.32 \text{ Diameter}$$

Contrary to tensile strength, elongation of stretched WPC-SDBS fibers at break was less than that of unstretched fibers (Table XIV). The regression equation for this relationship was:

TABLE XII

DIAMETER OF FINISHED FIBERS PREPARED WITH SODIUM DODECYL BENZENE SULFONATE AND WHEY PROTEIN CONCENTRATE

Fiber Type	Extraction Method	Detergent and WPC Concentration in Spinning Solution %	Time Elapsed Before Spinning (Hours) 0	6	24
			——diameter (cm x 10^{-4})[a,b]——		
Stretched	60% acetone	12	80.66a	71.81e	82.76k
		14	52.80b	53.96f	40.94m
	60% acetone + 5% KCL	12	78.98a	66.30e	74.30k
		14	45.41b	43.38f	41.32m
Unstretched	60% acetone	12	174.90c	181.05g	204.23n
		14	170.79d	162.86h	115.42p
	60% acetone + 5% KCL	12	184.69c	171.00g	189.83n
		14	130.73d	144.34h	111.26p

[a]Means of 10 measurements, 10 samples, and 2 replications.

[b]Means followed by the same letter are not significantly different at 0.05 level of probability.

TABLE XIII

TENSILE STRENGTH OF FINISHED FIBERS PREPARED WITH SODIUM DODECYL BENZENE SULFONATE AND WHEY PROTEIN CONCENTRATE[a]

Fiber Type	Extraction Method	Detergent and WPC Concentration in Spinning Solution %	Time Elapsed Before Spinning (Hours) 0	6	24
			—tensile strength (grams/cm^2)[d]—		
		12	25972.30a	27114.82a	19307.36a
	60% acetone	14	23187.93a	30280.85a	38066.22a
Stretched[b]		12	18690.34a	28984.75a	19519.11a
	60% acetone + 5% KCL	14	25238.33a	18889.59a	25478.93a
		12	8444.73b	8250.32b	7522.30b
	60% acetone	14	9244.15b	9818.08b	8776.52b
Unstretched[c]		12	8184.60b	8489.88b	10459.51b
	60% acetone + 5% KCL	14	9120.78b	7165.54b	9618.29b

[a]At 25°C and 70 ± 2 percent relative humidity.

[b]Means of 2 measurements, 10 samples, and 2 replications.

[c]Means of 1 measurement, 10 samples, and 2 replications.

[d]Means followed by the same letter are not significantly different at 0.05 level of probability.

TABLE XIV

ELONGATION OF FINISHED FIBERS PREPARED WITH WPC AND SODIUM DODECYL BENZENE SULFONATE[a]

Fiber Type	Extraction Method	Concentration of WPC and Detergent in Spinning Solution %	Time Elapsed Before Spinning (Hours) 0	6	24
			elongation (%)[d]		
Stretched[b]	60% acetone	12	1.80a	1.51a	1.63a
		14	1.79a	1.65a	1.56a
	60% acetone + 5% KCL	12	1.50a	1.78a	1.68a
		14	1.55a	1.47a	1.44a
Unstretched[c]	60% acetone	12	2.95b	2.90b	2.34b
		14	2.68b	2.90b	2.35b
	60% acetone + 5% KCL	12	3.28b	2.83b	3.15b
		14	2.15b	2.30b	1.95b

[a]At 25°C and 70 ± 2 percent relative humidity.

[b]Means of 2 measurements, 10 samples, and 2 replicates.

[c]Means of 1 measurement, 10 samples, and 2 replicates.

[d]Means followed by the same letter are not significantly different at 0.05 level of probability.

$$\text{Elongation} = 1.315 + 0.0071 \text{ Diameter}$$

This showed that the elongation of fibers increased with increased diameter. According to Moncrieff (120) highly oriented fibers usually have poor elongation because they have undergone a stretching operation to bring about their orientation. Therefore, poor elongation obtained with stretched fibers was not surprising since they were presumably more oriented than unstretched fibers.

Attempts to collect data concerned with the tensile strength and elongation of finished WPC-SLS fibers failed, because they were so brittle compared to WPC-SDBS fibers. Lundgren (102,104) proposed that fibers obtained with detergents containing short hydrocarbon chains would not be strong since low molecular weight sulfates and sulfonates lacked the behavior shown by high molecular weight sulfonates having long hydrocarbon chains. However, he did not present evidence to support his hypothesis.

6. COMPOSITION OF FINISHED FIBERS PREPARED WITH WPC AND DETERGENTS

Protein, residual detergent and phosphate (as orthophosphate) content of finished fibers prepared with WPC and SDBS are tabulated in Tables XV, XVI and XVII, respectively. Table XXII in the Appendix shows the composition of finished fibers prepared with WPC and SLS. Protein content of some fibers exceeding 100 percent in Table XV were probably due to errors in sampling, since the actual samples were very small.

TABLE XV

PROTEIN CONTENT OF FINISHED FIBERS PREPARED WITH SODIUM DODECYL BENZENE SULFONATE AND WHEY PROTEIN CONCENTRATE

Fiber Type	Extraction Method	Detergent and WPC Concentration in Spinning Solution (%)	Time Elapsed Before Spinning (Hours)		
			0	6	24
			Protein (%)[a,b,c]		
Stretched	60% acetone	12	98.68a	101.83a	99.19a
		14	92.57b	96.08b	97.54b
	60% acetone + 5% KCl	12	96.37a	97.79a	100.81a
		14	95.07b	100.91b	97.10b
Unstretched	60% acetone	12	95.34a	98.76a	96.47a
		14	93.10b	93.87b	92.90b
	60% acetone + 5% KCl	12	99.24a	96.55a	102.22a
		14	95.80b	95.65b	101.08b
Tow	60% acetone	12	107.07c	104.48c	100.83c
		14	98.72d	99.45d	99.83d
	60% acetone + 5% KCl	12	103.18c	101.32c	101.53c
		14	95.23d	99.72d	99.70d

[a]Means of 2 samples, and 2 replicates. [b]w/w on dry basis.

[c]Means followed by the same letter are not significantly different at 0.05 level of probability.

TABLE XVI

DETERGENT CONTENT OF FINISHED FIBERS PREPARED WITH SODIUM DODECYL BENZENE SULFONATE AND WHEY PROTEIN CONCENTRATE

Fiber Type	Extraction Method	Detergent and WPC Concentration in Spinning Solution %	Time Elapsed Before Spinning (Hours) 0	6	24
			detergent (%)[a,b,c]		
Stretched	60% acetone	12	0.54a	0.39a	0.39a
		14	0.31a	0.42a	0.52a
	60% acetone + 5% KCL	12	0.67a	0.51a	1.07a
		14	0.52a	0.81a	0.64a
Unstretched	60% acetone	12	1.17a	0.87a	0.86a
		14	0.42a	0.46a	0.50a
	60% acetone + 5% KCL	12	0.41a	0.40a	0.42a
		14	0.69a	0.49a	1.07a
Tow	60% acetone	12	0.87a	0.64a	0.84a
		14	1.02a	0.67a	0.93a
	60% acetone + 5% KCL	12	0.34a	0.26a	0.38a
		14	1.07a	0.73a	0.66a

[a]Means of 2 samples, 2 replications.

[b]w/w on dry basis.

[c]Means followed by the same letter are not significantly different at 0.05 level of probability.

TABLE XVII

PHOSPHATE CONTENT OF FINISHED FIBERS PREPARED WITH SODIUM DODECYL BENZENE SULFONATE AND WHEY PROTEIN CONCENTRATE

Fiber Type	Extraction Method	WPC and Detergent Concentration in Spinning Solution %	Time Elapsed Before Spinning (Hours) 0	6	24
			Phosphate (%)[a,b,c,d]		
Stretched	60% acetone	12	0.35d	0.27k	0.36k
		14	1.33e	1.28m	1.41m
	60% acetone + 5% KCl	12	0.28d	0.38k	0.27k
		14	1.37e	1.50m	1.46m
Unstretched	60% acetone	12	0.44f	0.37f	0.36n
		14	1.68g	1.82g	1.35t
	60% acetone + 5% KCl	12	0.38f	0.30f	0.46
		14	1.41g	1.54g	1.52t
Tow	60% acetone	12	1.00h	1.02p	1.20u
		14	1.30c	1.38r	1.36v
	60% acetone + 5% KCl	12	1.18h	1.11p	1.77u
		14	1.09c	1.54r	1.44v

[a]Determined as ortho-phosphate.

[b]w/w on dry basis.

[c]Means of 1 sample, 2 replicates.

[d]Means followed by same letter are not significantly different at 0.05 level of probability.

Examination of composition data and analysis of variance (Tables XXIII, XXIV and XXV, Appendix) indicated that time elapsed up to 24 hours before spinning did not affect the protein content of fibers prepared with either detergent. Fibers prepared with 12 percent WPC and SDBS had higher protein content than fibers prepared with 14 percent WPC and SDBS. WPC and SDBS concentration used and replication both had statistically significant effects ($P < 0.01$) on the protein content of finished fibers. Protein content of tows prepared with WPC and SDBS were significantly different from the protein contents of stretched and unstretched fibers prepared under the same conditions ($P < 0.05$). Protein concentration of unstretched fibers prepared with 14 percent WPC and SLS was significantly lower ($P < 0.05$) than stretched fibers and tows prepared under the same conditions (Tables XXII and XXIV, Appendix). Fibers prepared with 14 percent WPC and SLS had in general lower protein contents than fibers prepared with 14 percent WPC and SDBS (Tables XV and XXII, Appendix). Differences in the protein contents of fibers prepared with either detergent at 14 percent WPC and detergent level was due to detergent type used and was significant at the 0.01 level of probability (Table XXV, Appendix).

Residual detergent content of finished fibers averaged less than one percent (Tables XVI and XXII, page 85 and Appendix respectively). However, maximum amounts of SLS and SDBS permitted by FDA for use in food applications are lower (Table III page 28). Differences in the residual detergent content of fibers prepared with WPC and SDBS were not statistically significant (Tables XVI and XXIII, page 85 and Appendix

Lundgren's hypothesis implied that excess detergent was bound through non-polar forces to the detergent in the protein-detergent complex (101, 104) that extraction of detergent in the presence of an electrolyte was an ion-exchange reaction (104). He did not report the concentration of electrolyte which removed the maximum amount of detergent. The results of this study did not bear out Lundgren's conclusions.

Compared to the phosphate content of WPC (Table V page 55), residual phosphate concentration in finished fibers was lower (Tables XVII and XXII, Appendix) indicating that some phosphate was extracted in the process. Increased WPC and SDBS concentration in the spinning solution resulted in fibers with increased phosphate content (Table XVII). Variation in phosphate content of fibers due to WPC and SDBS concentration used, type of fibers produced and variation due to their interaction all were significant at the 0.001 level of probability (Table XXIII, Appendix). Phosphate content of WPC-SDBS fibers was also significantly affected ($P < 0.05$) by replication and by the interactions of time with fiber type and WPC and SDBS concentration (Table XXIII, Appendix). Differences in the phosphate content of WPC-SLS fibers was due only to fiber type (Table XXIV, Appendix), and phosphate content of unstretched fibers was significantly different ($P < 0.05$) than those of stretched fibers and tows (Table XXII, Appendix). The detergent type used in the preparation of 14 percent WPC-detergent spinning solutions significantly affected the phosphate concentration in finished fibers ($P < 0.05$) (Table XXV, Appendix). Phosphate content of fibers was also influenced by the interaction between detergent type and time elapsed before spinning at the 0.05 level of probability.

7. POSSIBILITIES FOR FOOD APPLICATIONS

Results of this study indicated that whey protein fibers containing less than one percent residual detergent can be prepared from WPC and detergent mixtures. Producing fibers with desired properties at a feasible cost would be an interesting contribution from engineers. Yet, any suggestion with respect to food uses of whey protein fibers such as production of simulated meat products should await their stability, safety and nutritional evaluation.

CHAPTER V

SUMMARY

An empirical attempt was made in this study to investigate the possibility of making protein fibers from whey protein concentrate (WPC) prepared from cottage cheese whey by a polyphosphate complexing process. WPC prepared and used in fiber studies had a low lactose (2.67 percent) and reasonably high protein (70.78 percent) content.

Fiber formation by WPC was studied by a wet-spinning process. Spinning solutions used were either aqueous alkaline WPC dispersions or aqueous alkaline WPC-anionic detergent mixtures.

Experimental results suggested that continuous fibers can be produced from aqueous alkaline WPC dispersions. However, fibers produced were not strong enough to be of any practical value. Twelve and 14 percent aqueous alkaline WPC solutions containing equal concentration (based on weight of WPC) of the detergents, sodium lauryl sulfate (SLS) or sodium dodecyl benzene sulfonate (SDBS), in the presence of 0.5 percent β-mercaptoethanol (based on the volume of spinning solution) formed continuous fibers with excellent handling properties. Detergent then was extracted with 60 percent aqueous acetone or 60 percent aqueous acetone containing 5 percent potassium chloride.

WPC-detergent fibers put into water before detergent extraction disintegrated in a short time. Fibers after the extraction of detergent were not affected by boiling in water for 30 minutes. The average water absorbtion of detergent extracted fibers was 1.23 times the dry weight.

Tensile strength, elongation properties and the diameter of detergent extracted fibers were significantly affected by the stretching operation. Stretching resulted in fibers of smaller diameter. Tensile strength of fibers was increased and elongation was decreased.

Time elapsed up to 24 hours between the preparation of spinning solution and fiber production did not result in a decrease in the protein content of finished fibers. Presence of potassium chloride did not appear to enhance the detergent extracting capacity of 60 percent aqueous acetone. However, acetone treatment removed most of the detergent present in the fibers. Overall mean composition of WPC-SDBS fibers was 98.5 percent protein, 0.6 percent SDBS and 1.0 percent phosphate, whereas, WPC-SLS fibers contained 92.6 percent protein, 1.3 percent SLS and 1.2 percent phosphate.

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APPENDIX

TABLE XVIII

DIFFUSION OF COAGULATING BATH INTO SPINNING SOLUTION

Time Interval (Minutes)	Spinning Solution Made With								
	WPC (%)			WPC and SDBS (%)			WPC and SLS (%)		
	10	12	14	10	12	14	10	12	14
	diffusion (cm)[a]								
0 - 10	0.173	0.144	0.135	0.116	0.107	0.068	0.116	0.081	0.078
10 - 20	0.076	0.075	0.075	0.052	0.054	0.053	0.062	0.061	0.044
20 - 30	0.057	0.058	0.058	0.041	0.043	0.037	0.049	0.041	0.035
30 - 40	0.049	0.049	0.048	0.035	0.040	0.033	0.034	0.036	0.029
40 - 50	0.045	0.045	0.045	0.035	0.039	0.029	0.031	0.028	0.027
50 - 60	0.041	0.041	0.039	0.035	0.032	0.027	0.028	0.024	0.023
60 - 70	0.037	0.036	0.037	0.035	0.032	0.024	0.028	0.021	0.021
70 - 80	0.034	0.034	0.036	0.035	0.032	0.024	0.028	0.021	0.021
Total	0.512	0.482	0.471	0.384	0.379	0.295	0.376	0.313	0.278

[a]Means of 3 samples.

TABLE XIX

APPARENT VISCOSITIES AT VARIOUS TIME INTERVALS FOR SPINNING SOLUTIONS PREPARED WITH DETERGENTS AND WHEY PROTEIN CONCENTRATE

Detergent	Detergent and WPC Concentration (%)	Time (Hours) 0	6	24
		apparent viscosity (centipoise)[a,b]		
SDBS	10	8.34a	7.97e	7.59k
	12	94.06b	60.41f	55.11z
	14	548.33c	429.33g	360.00m
SLS	10	9.30a	8.93e	8.70k
	12	52.94b	37.00f	33.83z
	14	391.87d	320.55h	270.83n

[a]Means of 3 samples, and 3 replications.

[b]Means followed by the same letter are not significantly different at 0.05 level of probability.

TABLE XX

SUMMARY OF ANALYSIS OF VARIANCE FOR THE EFFECTS OF WPC AND DETERGENT CONCENTRATION, DETERGENT TYPE AND TIME ON THE APPARENT VISCOSITIES OF SPINNING SOLUTIONS PREPARED WITH WPC AND DETERGENTS

	Source	D.F.	M.S.
A.	WPC and Detergent concentration	2	2295886***
B.	Detergent type	1	95562
	A x B	2	51952
C.	Replication	2	7359
	Error A[a]	10	39326
D.	Time	2	52581***
	A x D	4	30711***
	B x D	2	3094
	A x B x D	4	1415
	Error B[b]	12	863
	Residual	120	62

***$p<0.001$.

[a] [A x C + B x C + A x B x C].

[b] [C x D + A x C x D].

TABLE XXI

SUMMARY OF ANALYSIS OF VARIANCE FOR THE EFFECTS OF WPC AND DETERGENT CONCENTRATION, FIBER TYPE, DETERGENT EXTRACTION METHOD AND TIME ELAPSED BEFORE SPINNING ON THE PHYSICAL PROPERTIES OF STRETCHED AND UNSTRETCHED FINISHED FIBERS PREPARED WITH WPC AND SODIUM DODECYL BENZENE SULFONATE

Source	D.F.	Diameter ($cm \times 10^{-4}$)	Tensile Strength (g/cm^2)	Elongation %
		M.S.		
A. WPC and Detergent concentration	1	165236	442858062	11.27
B. Fiber type	1	1212955**	31656938035*	115.66*
A x B	1	7567	278122217	6.86
C. Extraction	1	9839	601924011	0.11
A x C	1	1921	420790205	7.27
B x C	1	1776	693161782	0.31
A x B x C	1	1933	135884070	3.00
D. Replication	1	17246	4699725899	10.54
Error A[a]	6	38748	2543171334	9.15
E. Time	2	2210	90536532	2.51
A x E	2	17278***	641630242	1.33
B x E	2	1022	106806210	1.28
C x E	2	179	28579770	1.42
A x B x E	2	6987*	650193098	1.20
A x C x E	2	3519	540284631	0.09
B x C x E	2	73	92005632	1.25
A x B x C x E	2	1509	339368709	0.21
Error B[b]	8	838	731516352	3.84
Residual	441	489	127439340	0.73

TABLE XXI (continued)

*P<0.05.

**P<0.01.

***P<0.001.

[a][A x D + B x D + A x B x D + C x D + A x B x C x D].

[b][D x E + A x D x E + B x D x E + C x D x E].

TABLE XXII

COMPOSITION OF FINISHED FIBERS PREPARED WITH 14 PERCENT WPC AND SODIUM LAURYL SULFATE

Fiber Type	Extraction Method	Time Elapsed Before Spinning (Hours)	Protein	Detergent	$PO_4^{\equiv}$ (Ortho)
			%[a,b,c]		
		0	94.32a	1.00c	1.17z
	60% acetone	6	93.87a	0.98c	0.98z
		24	93.44a	0.69d	1.31z
Stretched		0	90.04a	0.98c	0.90z
	60% acetone + 5% KCl	6	96.95a	0.96c	1.34z
		24	93.66a	0.59d	1.30z
		0	89.00b	1.29e	1.09t
	60% acetone	6	89.56b	1.49e	1.00t
		24	88.58b	1.40f	0.65t
Unstretched		0	93.90b	1.54e	0.77t
	60% acetone + 5% KCl	6	91.36b	1.70e	1.10t
		24	92.89b	1.03f	0.85t
		0	92.15a	1.49e	1.44z
	60% acetone	6	93.61a	1.46e	1.17z
		24	93.51a	1.68f	1.47z
Tow		0	91.91a	1.59e	1.44z
	60% acetone + 5% KCl	6	92.78a	2.16e	1.31z
		24	95.08a	1.00f	1.54z

TABLE XXII (continued)

[a]w/w on dry basis.

[b]Means of 2 samples and 2 replications.

[c]Means within the column followed by the same letter are not significantly different at 0.05 level of probability.

TABLE XXIII

SUMMARY OF ANALYSIS OF VARIANCE FOR THE EFFECTS OF WPC AND DETERGENT CONCENTRATION, FIBER TYPE, DETERGENT EXTRACTION METHOD AND TIME ELAPSED BEFORE SPINNING ON THE COMPOSITION OF FINISHED FIBERS PREPARED WITH 12 AND 14 PERCENT WPC AND SODIUM DODECYL BENZENE SULFONATE

	Source	D.F.	Protein	Detergent	$PO_4^{\equiv}$
			%		
			M.S.		
A.	WPC and SDBS concentration	1	182.596**	0.044	11.282***
B.	Fiber type	2	112.559*	0.112	1.179***
	A x B	2	5.538	0.262	1.932***
C.	Extraction method	1	8.750	0.026	0.027
	A x C	1	21.934	0.693	0.033
	B x C	2	37.568	0.463	0.067
	A x B x C	2	3.349	0.320	0.057
D.	Replication	1	154.704**	0.782	0.283*
	Error A[a]	9	14.560	0.183	0.049
E.	Time	2	17.187	0.130	0.055
	A x E	2	13.389	0.011	0.098*
	B x E	4	12.393	0.049	0.071*
	C x E	2	16.709	0.028	0.067
	A x B x E	4	6.899	0.092	0.036
	A x C x E	2	12.499	0.046	0.009
	B x C x E	4	8.603	0.039	0.039
	A x B x C x E	4	4.340	0.057	0.025
	Error B[b]	10	20.71	0.138	0.016
	Residual	16	9.487	0.056	0.016

TABLE XXIII (continued)

*P<0.05.

**P<0.01.

***P<0.001.

[a][A x D + B x D + C x D + A x B x D + A x C x D + B x C x D].

[b][D x E + A x D x E + B x D x E + C x D x E].

TABLE XXIV

SUMMARY OF ANALYSIS OF VARIANCE FOR THE EFFECTS OF FIBER TYPE, DETERGENT EXTRACTION METHOD AND TIME ELAPSED BEFORE SPINNING ON THE COMPOSITION OF FINISHED FIBERS PREPARED WITH 14 PERCENT WPC AND SODIUM LAURYL SULFATE

Source	D.F.	Protein	Detergent	$PO_4^{\equiv}$
		%		
		M.S.		
A. Fiber type	2	27.095*	1.603*	0.706*
B. Extraction method	1	12.297	a	0.008
A x B	2	14.280	0.007	0.004
C. Replication	1	43.913**	0.045	0.067
Error A[b]	5	2.659	0.256	0.105
D. Time	2	4.523	0.473*	0.009
A x D	4	6.085	0.024	0.117
B x D	2	2.810	0.367	0.126
A x B x D	4	7.615*	0.115	0.028
Error B[c]	8	1.584	0.095	0.051
Residual	4	7.540	0.041	0.082

*P<0.05.

**P<0.01.

[a]M.S.<0.001.

[b][A x C + B x C + A x B x C].

[c][C x D + A x C x D + B x C x D].

TABLE XXV

SUMMARY OF ANALYSIS OF VARIANCE FOR THE EFFECTS OF DETERGENT TYPE, FIBER TYPE, DETERGENT EXTRACTION METHOD AND TIME ELAPSED BEFORE SPINNING ON THE COMPOSITION OF FINISHED FIBERS PREPARED WITH 14 PERCENT WPC AND DETERGENTS[a]

Source	D.F.	Protein	Detergent	$PO_4^{\equiv}$
		%		
		M.S.		
A. Detergent type	1	335.491**	6.857***	1.350**
B. Fiber type	2	50.781	1.546***	0.128
A x B	2	11.675	0.375	0.711*
C. Extraction method	1	39.694	0.123	0.003
A x C	1	1.799	0.103	0.005
B x C	2	30.459	0.041	0.029
A x B x C	2	5.750	0.067	0.015
D. Replication	1	6.078	0.188	0.350
Error A[b]	9	20.411	0.173	0.091
E. Time	2	28.828	0.117	0.043
A x E	2	6.150	0.402*	0.032
B x E	4	10.070	0.036	0.106*
C x E	2	6.150	0.197	0.156
A x B x E	4	1.320	0.104	0.050
A x C x E	2	0.108	0.171	0.020
B x C x E	4	10.381	0.102	0.042
A x B x C x E	4	7.120	0.076	0.020
Error B[c]	10	8.398	0.082	0.038
Residual	16	12.698	0.247	0.045

TABLE XXV (continued)

[a]SDBS and SLS.

[b][A x D + B x D + C x D + A x B x D + A x C x D + B x C x D].

[c][D x E + A x D x E + B x D x E + C x D x E].

*P<0.05.

**P<0.01.

***P<0.001.

VITA

Turker Asan was born in Denizli Province, Turkey on November 1, 1941. He attended Cal Elementary School and Denizli Lycee and graduated in 1958. He entered the University of Ankara, Turkey in 1958. In June of 1964, he received a Bachelor of Science degree in Veterinary Medicine.

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In February of 1969, he entered Columbia University School of Physicians and Surgeons. In the Fall of 1970, he received a Master of Science degree in Nutrition.

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