HGCA

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INDUSTRIAL MARKETS FOR UK-GROWN CROP POLYSACCHARIDES

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by

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CONTENTS

BACKGROUND

Crop polysaccharides, of which starch is the second most commonly found form, have been identified by LINK as a priority area within the Crops for Industrial Use programme.

Starch is the principal storage carbohydrate material of plants and as such accounts for 80% of the calorific value of the human diet. It is also a useful and important industrial commodity with a wide range of non-food applications. Approximately 37% of European starch production is estimated to be for industrial, non-food uses in comparison to 60% in the USA and 20% in other parts of the world. UK consumption of starch for industrial use accounted for 216 221 tonnes in 1993/94. Much of this starch is modified by physical, chemical or enzymatic methods in order to give it the specific characteristics required by a particular industry. In addition individual sectors may prefer starch from a particular botanical source for certain applications.

The different industrial uses of starch vary in their state of development. Some are well established uses, e.g. paper production. Some are new uses at an early stage of development, e.g. pharmaceuticals, while others are in decline, e.g. textiles.

This report has been commissioned to identify more precisely:

1. current industrial applications of crop starch
2. present market size and the potential for growth of established starch-using sectors
3. potential new industrial applications for crop starch particularly in relation to the opportunities for adding value
4. current limitations to the use of UK crop starch and the properties required
5. the conditions that would allow greater utilisation of this material
6. opportunities for UK agriculture

This study addressed these issues through an extensive review of published and unpublished literature, detailed discussions with key industrial companies and research centres and the economic assessment of investment opportunities. Some limited market research was also undertaken to help evaluate market opportunities. Developments in starch technology outwith the UK were also actively researched and incorporated into the final report to give a comprehensive review of the starch industry.

Chapter 1 gives a description of the UK starch industry, and current UK markets for crop starch are identified and quantified. Chapter 2 defines starch and gives a brief description of its composition and synthesis within the plant. The implication for industrial starch production from modifying the pathway of synthesis is indicated. Chapter 3 establishes current sources of starch and describes the properties of starches that can be commercially produced within the UK. Attention is drawn to the potential that exists to modify starch produced within plants through crop management and genetic modification.

The primary processing of crops to produce native or raw starch is described in Chapter 4. In Chapter 5, the economics of starch production from potato, maize and wheat are presented, together with the opportunities for their development in the UK. Chapter 6 describes the secondary processing of starch to produce a wide range of modified starches that meet the particular requirements of individual markets. These markets and their requirements are considered in some detail in Chapter 7. For each sector, estimates of market size are presented and quality requirements set out. The potential development of these markets is reviewed and critical requirements for greater utilisation of starch for these applications are identified.

A description of these requirements is presented in Chapter 8 in the context of developing the UK industrial starch industry and in the light of future developments in both EU and world trade policy.

EXECUTIVE SUMMARY

The UK starch industry

1. UK starch production is 750 000 tonnes, of which 75% is from imported maize. The remaining production is principally from home grown wheat. Approximately 25% of UK supplies is used for industrial purposes, with paper and cardboard accounting for 59% of this use. Industrial uses of total supplies accounted for 13% of wheat starch, 21% of maize starch and 82% of potato starch. This makes maize the most important industrial source by volume (57%) in the UK as with the rest of Europe (54%).

Starch and its synthesis

2. Starch occurs as dense, semi-crystalline, water-insoluble granules. The size and shape of starch granules vary widely not only between different species, but also between varieties of the same species, and even between cells of the same plant.

3. The major components of starch are 2 types of glucose polymers, amylose and amylopectin. Amylopectin is more branched and consists of a far greater number of glucose residues than amylose. There is a great variation in starch from different crop sources, which is exemplified by differences in the ratio of amylose to amylopectin.

4. The synthesis of starch involves the formation of $\alpha(1 \rightarrow 4)$ glucopyranose chains, their extension to give amylose, their branching to give amylopectin, together with the correct positioning of the amylose and amylopectin to give the final granule. Starch synthesis is controlled by the availability of the initial substrate, glucose phosphate, and the relative activities of the different enzymes responsible for the conversion of this glucose phosphate to starch. The relative importance of these different factors in controlling starch synthesis is not yet known.

Sources of starch and their characteristics

5. Most of the starch processed by industry comes from a relatively small number of crops: maize, potato, wheat, tapioca and waxy maize. Maize, potato and wheat starches are used for both food and non-food applications. Of these crops only wheat and potatoes can be grown in the UK at present. Maize dominates the starch industry in Europe, but wheat starch production has increased since 1983 which is attributed to the increase in demand for the co-product gluten.

6. Starch from different sources may vary with regard to several basic characteristics. These include starch granule properties, composition of starch granules, relative amylose and amylopectin levels, gelatinisation characteristics, properties of starch pastes and properties of starch films.

7. Potato starch granules are large and oval or egg-shaped. Potato starch has both a relatively low lipid and nitrogen-containing compound content but a high level of bound phosphorus. It has a relatively low pasting temperature and a high solubility in water, both desirable factors which can be related to its low lipid and high phosphorus content. Potato starch has an amylose: amylopectin ratio of 22:78. Amylose-free or

"waxy" varieties have been produced using biotechnological techniques and are presently undergoing field trials in The Netherlands.

8. Maize and wheat starch are similar in many respects. Differences lie principally in the size and shape of the granules. Maize starch granules are either spherical or polygonal and wheat starch granules are flat, spherical or elliptical. Granules from wheat, barley or rye can be separated into different classes based on size. Wheat and maize starches have a high lipid content and high content of nitrogenous substances which may have some undesirable effects on properties. Separation of wheat starch proteins may be desirable as this fraction, gluten, also has commercial value. The amylose: amylopectin ratio is similar for wheat and maize starches at approximately 27:73.

9. Oat starch has round, relatively small granules, with a narrower granule size distribution than maize or wheat. These properties may mean that it is particularly suited to certain applications. Barley starch has round or elliptical granules. Processing of barley starch is easier than wheat starch as it does not require gluten separation, but without the valuable gluten by-product it is less likely to be commercially viable. Rye and triticale starch do not seem to have any distinctive features which differentiate them from commonly grown UK cereals.

10. Of the new starch crops available, quinoa and amaranth are of interest. Quinoa starch has an extremely small granule size and a very low amylose content. The presence of saponin anti-nutrients may restrict the use of the grain pericarp by-product as an animal feedstuff. Amaranth starch granules are round or dodecahedral and very small with a very low amylose content. However, agronomic potential of amaranth in the UK is limited.

11. Characteristics of starch vary with the site of the crop, weather and management practices adopted. This will influence suitability for industrial processes but is not exploited. Genetic modification of crops both by conventional breeding and genetic engineering techniques offer a wide range of potential industrial starches in the medium to long term. However, the practicalities of processing a multitude of industrial starch types suggest that developments should be restricted to crop types producing "part modified" starches which can then be processed for the various industrial markets.

12. It is not clear whether plants can be genetically engineered to produce more starch. Fulfilment of this aim depends on the number of enzymes that control starch synthesis. There are good prospects for changing the type of starch formed by a plant with the large range of natural variation in starches found in crop plants. This can be done by conventional breeding or by genetic engineering. It seems likely that production of plants with no amylose will be possible. However, production of starch with no amylopectin is less probable because of the important role of amylopectin in determining granule structure.

Primary processing

13. Production of starch from potatoes is a seasonal operation because potatoes, having a high moisture content, deteriorate in quality with storage. Starch production from potatoes involves storage, washing, disintegration, extraction, refining and drying. Potato starch by-products are fibre and potato juice - both of low value, but potato starch dominates the yield and value in dry matter terms.

14. Cereals can be dried and stored easily allowing cereal starch processing throughout the year. Both maize and wheat gluten as by-products contribute significantly to the profitability of the operation. Wheat processing initially involves milling followed by processing by the Martin method, the batter process or by an alkali process to obtain the starch. Starch is separated according to granule size into 3 phases; 'A' starch, 'B' starch and the remaining light phase. The gluten by-product is used principally in the food industry.

15. Maize starch is processed using a wet milling process involving grain steeping, germ separation, milling and sieving and gluten separation.

Starch production economics

16. The manufacture of native starch within the EU is dependent on the payment of production refunds to allow EU starch to compete with imports. EU potato production receives additional support per tonne of starch produced in the form of "fixed premiums" limited to 1.592 million tonnes and distributed principally to Germany, Holland, France and Denmark.

17. The processing margin for the starch industry is calculated as wheat starch £56/tonne, maize £53/tonne and potatoes £18/tonne. The margin for potato starch equals the EU subsidy received.

18. Quota restrictions of EU subsidy are likely to prevent the development of a UK potato starch industry. UK potato growers will not find it attractive to grow the crop without the compensation payments given to other producing countries. Development of a UK starch industry will need therefore to concentrate on the opportunities presented by wheat starch, which competes with maize and which has a superior margin. A wheat processing plant with a capacity of 100 000 tonnes would take up to 14 000 ha of set-aside, supply one third of the UK's gluten imports and supply over 6% of the UK's unmodified starch requirements.

Secondary processing

19. Starch manufacturers add considerable value to native starch with secondary processing to give a wide range of modified starches to meet specific market requirements. Potato starch has traditionally been regarded as having superior properties to cereal starch but developments in secondary processing will allow the production of cereal starch with similar properties at a lower price. The development of biochemical methods of modification may reduce chemical use and processing requirements.

20. Starch derivatives are divided according to processing method. Group I starch derivatives are known as tank products and require cooking before use. They are the basic group of starch derivatives which are used in food, textile, paper and adhesive applications. Tank products include oxidised starches, oxidised acetylated starches, cross-linked starches and oxidised starch ethers.

21. Group II starches are cold water soluble products and consist of simple pre-cooked starch products. Highly substituted starch ethers (Group III) are more sophisticated treated products. Group IV products are roasted starches, or dextrins or roasted starch ethers. Groups II - IV have a wide range of specialist non-food applications.

Industrial markets for starch

22. **Paper and board industry**

The paper and board industry is the biggest non-food starch-using sector, taking 59% of UK industrial starch. Starch is used in several segments of the paper manufacturing process. Paper use is closely linked to the economic situation. Between 1990 and 1993 paper use increased slightly, with starch use in line with this.

An SAC survey of paper manufacturers obtained a high level of response - 57% of the UK's 1993/94 paper and board sector use. It showed that 51.2% of total starch use was in surface sizing, followed by 30.4% in wet end and 16.3% in unspecified use, 1.1% in coating and 1% in ply bonding. The main starch source was maize (36.7%), followed by potatoes (23.3%), wheat (17.4%) and waxy maize (0.51%). Potato starch is preferred because of quality, but maize and wheat are often chosen because of lower cost. Manufacturers tend to purchase cationic starch for use at the wet end but buy native starch for on-site modification to adjust viscosity for sizing. Both modified and unmodified starches can be used for coating.

Demand for starch by the paper industry may increase due to higher levels of incorporation of starch in paper as a filler. Synthetic products compete with starch use as a binder and retention aid.

23. **Starch-based components of detergent manufacture**

Consumer concern over environmental issues has led to increasing interest in starch derived products for the detergents industry. Surfactants are the primary cleaning agents within detergents. Plant based carbohydrates may be used to provide the water soluble portion of detergents and to form APGs (alkylpolyglycosides) which are considered to have a range of environmental qualities. Commercialisation of surfactants depends on their price relative to synthetics.

Builders and co-builders or sequestering agents buffer the wash medium, soften the water and disperse soil particles removed during washing. Starch derived products have shown satisfactory technical qualities but there is a lack of a suitable economic process for their production.

Bleaching boosters allow bleaching to take place at lower temperatures. Starch derived products for this purpose are under investigation.

For all uses within the detergents area, source of starch is not important as modified starch derivatives are used. However, it must be ensured that the biodegradability of starch products, which is their attraction for detergent use, is not lost during modification. Much development work on use of starch in detergents is being carried out. The detergents sector is a relatively new market with potential to be a very large consumer of starch products. The size of the market that is achieved will depend on environmental pressures and legislation and also commercial pressures on price.

24. Flocculation products for water purification

Starch based products have traditionally been used by the water treatment industry as a coagulant or flocculant aid. Potato starch is associated with better performance than other types because of its high potassium content. Starch based products have been displaced to a large extent by synthetic polyelectrolytes because of the superior performance and lower dosage rates required of the latter. Starch flocculants are however preferred in some countries. The biodegradability of starch may be undesirable for this use as it increases the biological oxygen demand.

25. Textiles

The textiles industry is a traditional market for starch but now only accounts for 0.36% and 1.4% of the industrial starch market in the EU and UK respectively. There are 3 main applications of starch: sizing, where potato starch is used, printing, for which cereal starch is preferred, and finishing, which uses dextrins and degraded starches. The decline noted for starch consumption for this market is due to the overall decline in the European textiles industry and the increased use of synthetic sizing products. Synthetic sizing products are more expensive, but have a superior performance as compared to starch products. Synthetics are used where certain sophisticated finishes are required. Starch products still retain a share of the textiles sector market because of their lower cost than synthetics.

26. Plastics

Use of starch for the production of plastics has been researched for a considerable time. The biodegradablity of these products has led to considerable recent interest. Starch is used in 3 major plastic types: loaded products, polymer mixtures and thermoplastic starches. High amylose content and small granule size are desirable qualities of starch for use in plastic production. Modification may be necessary to make hydrophilic native starch more compatible with hydrophobic plastics.

The present market for starch in plastic materials is very small - 1.7% and 3% of industrial starch use in the EU and UK respectively. The low price and high quality of traditional petrochemical products, as well as developments in recycling plastics and the effects of the recession, which discourages environmentally beneficial practices at a financial cost, are factors which are inhibiting the development of biodegradable plastics. Estimates of the future market depend on consumer attitudes, legislative and regulatory action and the success of recycling and other solid waste programmes. The emphasis on prevention policies in waste management have led to the suggestion that degradable plastics would be most valuable in niche markets.

27. Adhesives

Adhesives are a traditional application for starch. Starch based adhesives are primarily used for paper bonds and the most important sector for their use is corrugated board production. Starch based adhesives have faced strong competition from high performance synthetic products, and are unlikely to maintain their current position within the adhesives market.

28. Starch for mineral oil drilling

Starch can be used in the oil industry as a drilling aid. Starch can be included in a number of different formulations of water based drilling fluids. The amount of drilling fluid used varies substantially with the number of wells in operation. It is estimated that 40% of drilling fluids are water based and of these 5 - 10% contain starch at 1 - 3% concentration, indicating a maximum annual market requirement of 400 tonnes based on 1987 drilling figures. The largest limitation for use of starch-containing drilling fluids is the restricted range of conditions in which these fluids can be used. Modification of starch for high temperature use would increase its market potential significantly.

29. The use of starch in the agrochemical industry

Starch is of interest in the agrochemical industry as an encapsulation agent for pesticides, and for the production of aqueous base pesticide formulations. However, the potential for starch in this sector is unclear.

30. Pharmaceuticals

Starch can be used in the pharmaceuticals industry for coating and dusting tablets, binding the components of the tablets and production of active ingredients. This is a high value, low volume market which is considered to have good potential. Development of active ingredients may be restricted by the high investment required for registration of new products.

31. Cosmetics and toiletries

Starch and starch derivatives could potentially be used for the production of a wide range of cosmetics and toiletry products. The use of sorbitol in toothpaste is an example of a well established use of a starch derivative in this sector. There is potential to develop the use of starch and starch derivatives in this sector. This is likely to be a low volume, high value market.

32. Development of the UK industrial starch industry

Quota restrictions on the allocation of EU support payments prevent the development of a UK potato starch industry. Without EU compensation payments, UK potato growers would not find it attractive to grow starch potatoes for industrial markets. Emulation of the Dutch starch potato industry would be difficult because of the large size of starch factory required for economic processing and the intensity of potato production required within a farming locality to satisfy throughput without excessive transport costs. Development of the UK industrial starch industry will need to concentrate on the opportunities presented by cereals - particularly wheat.

RECOMMENDATIONS

1. As EU quota restrictions inhibit the establishment of a UK potato starch industry, developments in the UK industrial starch industry will need to concentrate on cereals.

2. Cereal starches are securing some new industrial markets despite certain quality limitations simply on the basis of cost competitiveness. There is a major role for government to play in supporting basic research which is likely to maintain or improve the cost competitiveness of UK cereal starch production.

3. Further work is required to elucidate the precise roles and relative importance of the enzymes responsible for controlling starch synthesis in order to allow variability of starch synthesis to be exploited commercially.

4. There is a need to assess the importance of climate, growing location and crop management on the potential for influencing starch quality and industrial potential.

5. Genetic modification, both by conventional breeding and genetic engineering techniques, offers the opportunity for producing radically different starch qualities. However, the expense of these techniques makes it vital that a close dialogue is maintained with starch industry processors and users to ensure that the varietal types being developed will cater for a market of sufficient size and profitability.

6. A watching brief needs to be maintained on the potential for new starch sources. These may include both new crops (e.g. quinoa) and non traditional starch crops which grow well in the UK. Oats in particular merits further investigation of its industrial potential.

7. Of all the starch-using sectors, paper, surfactants, cosmetics and pharmaceuticals offer the greatest potential for wealth creation through UK starch use and product development. Further research is required, particularly in the paper industry, to ensure that it is UK grown starch crops which are selected by processors and manufacturers. Research on product development is the key to maximising the potential of the high value pharmaceuticals, cosmetics and surfactants markets.

CHAPTER 1 THE UK STARCH INDUSTRY

This chapter indicates the total quantities and botanical sources of starch currently processed in the UK and the EU. The split in use between food and non-food markets is given for each botanical source of starch. Non-food use is further divided into uses which fall into a number of categories used by the intervention board for classifying products which qualify for "production refunds". These refunds are paid to non-food users of starch to compensate for the high internal EU price of raw materials (see Chapter 5). Individual markets are studied in detail in Chapter 7.

Output from UK starch processors rose over the five-year period to 1993/94 to reach approximately 750 000 tonnes of starch over the 12 months to 30 June 1994 (Table 1.1). Within this total, approximately 75% or 560 000 tonnes was maize starch produced from approximately 900 000 tonnes of imported maize. The remaining 25% or 190 000 tonnes was wheat starch produced from approximately 400 000 tonnes of principally home-grown wheat.

Starch imports in 1993/94 of approximately 133 000 tonnes gave a total UK starch supply estimated at 883 000 tonnes before account is taken of stock changes and exports. UK starch exports are generally small at around 6 000 tonnes per annum and have little impact on the market. Table 1.1 shows the utilisation of the UK starch supply in food and industrial markets by starch type, in 1993/94.

An estimated 75% of UK total starch supplies was utilised by the food industry and 25% or approximately 216,000 tonnes was used for industrial purposes. By far the most important industrial outlet was the paper and cardboard industry which took 127 845 tonnes of starch in 1993/94, representing 59% of the total industrial market in the UK. Second and third in importance were the use of starch for production of organic chemicals (15%) and albuminoid substances (11%).

Only 13% of wheat starch (27,801 tonnes) was utilised by industrial starch users. This compared with 21% of maize starch (123,324 tonnes) and 82% of potato starch (65,043 tonnes). Maize starch was by far the most important source of industrial starch by volume - representing 57% of total supplies. A similar situation exists elsewhere in the European Union. Table 1.2 shows the industrial utilisation of starch in 11 of the EU member states; maize starch supplies 54% of the EU industrial market compared to 57% in the UK.

Table 1.2 also shows the industrial outlets for starch within the EU (11). As in the UK, the paper and cardboard industry is of major importance, taking 39% of industrial starch. Unlike the UK however, esterified and etherified starch markets are of more importance taking 34% of industrial starch compared with only 4% in the UK. Organic chemical markets are of similar importance representing 15% of the total market in both the UK and the EU. Use of starch for the production of albuminoid substances is relatively more important in the UK than elsewhere in the EU.

Table 1.1 UK starch processing and utilisation 1993/94 (tonnes)

	wheat	maize	potato	other(1)	Total
UK output	190 000	560 000	0	0	750 000
Imports	17 173	34 838	79 177	2 421	133 609
Total Supply	207 173	594 838	79 177	2 421	883 609
Food use	179 372 (87%)	471 511 (79%)	14 143 (18%)	2.362 (98%)	667 438 (75%)
Industrial use	27 801 (13%)	123 324 (21%)	65 043 (82%)	50 (2%)	216 221 (25%)
Sector					
organic chemicals	5 693	24 332	1 719		31 744
pharmaceutical		4 880			4 880
organic surfactants		2 912		50	2 962
starch ethers & esters		4 841	4 779		9 620
enzymes		230			230
albuminoid substances(2)		12 354	12 346		24 700
industrial chemicals	911	6 320	224		7 455
plastic products		6 178	599		6 777
paper & cardboard	21 197	61 272	45 376		127 845
cotton		8			

Source: HGCA. Weekly Digest Vol. 21, No. 31, 6/2/95
European Commission

(1) Rice, manioc and others.
(2) Casein, caseinates and other casein derivatives, casein glues (also known as cold glues).

Table 1.2 EU (11) industrial starch market 1993/94 (tonnes)

	wheat	maize	potato	other(1)	Total
Total industrial use	325 527 (13.6%)	1 305 046 (54.5%)	762 706 (31.9%)	1 000	2 393 000
Sector					
carrageenan	-	1 575	-	-	1 575
organic chemicals	51 098	297 115	15 448	-	363 661
pharmaceutical	939	47 180	360	-	49110
organic surfactants	868	6 970	6	0	7 849
animal glues	-	101	2 086	-	2 187
starch ethers & esters	41 500	347 194	423 120	68	811 882
glues (2)	518	868	2 159	31	3 576
enzymes	4 715	26 197	11 832	-	42 545
albuminoid substances	26	32 096	13 031	-	45 153
industrial chemicals	5 811	81 792	3 289	-	90 892
plastic products	6 937	21 572	11 749	25	40 283
paper & cardboard	213 087	439 900	276 238	3	929 228
cotton	27	1 848	3 588	-	5 462
special textiles		9			0

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(1) Rice, manioc and others.

(2) Prepared glues and other prepared adhesives; products suitable for use as glues or adhesives, put up for retail sale as glues or adhesives not exceeding a net weight of 1 kg.

Source: European Commission

The manufacture of native starch from wheat and maize in the UK is concentrated within four companies.

- Cargill
- Tunnel
- Cerestar
- ABR

A number of these companies are capable of processing both wheat and maize. Others have dedicated plants suitable for only wheat or maize. New investment is expected to increase wheat-processing capacity. This will allow processors to move gradually away from a reliance on imported maize and encourage an increase in wheat starch manufacture. This is encouraged by superior wheat processing margins relative to maize and potatoes (see Chapter 5).

CHAPTER 2 STARCH AND ITS SYNTHESIS

This chapter describes where starch is found, its composition, structure and variation in characteristics. The pathway of starch synthesis within the plant is described, indicating how changes in this pathway may result in starches with differing industrial qualities.

2.1 Occurrence of starch

Starch is the dominant reserve material of plants and an important part of the human diet. In higher plants starch is confined to plastids: chloroplasts in leaves and, typically, amyloplasts in storage organs such as seeds and tubers. Starch occurs as dense, semi-crystalline, water-insoluble granules. These consist of alternating amorphous and semi-crystalline growth rings (120-400 nm thick). The size and shape of starch granules vary widely, not only between different species but also between varieties of the same species, and even between cells of the same plant. Granules can be round, oval, irregular or elongated, and can range from 1 to 100 μm in length.

2.2 Composition and structure of starch

2.2.1 Major constituents

Starch granules vary in composition as well as in size and shape. The major components of starch are 2 types of glucose polymers - amylose and amylopectin. Roughly 15-30% of starch is amylose and the rest is amylopectin. Amylose consists of 1000 to 6000 glucopyranose units and has 2 components, linear molecules of $\alpha(1\rightarrow4)$-linked glucose residues (Fig 2.1), and lightly branched molecules made of a small number of long $\alpha(1\rightarrow4)$-linked glucose chains joined by $\alpha(1\rightarrow6)$- links.

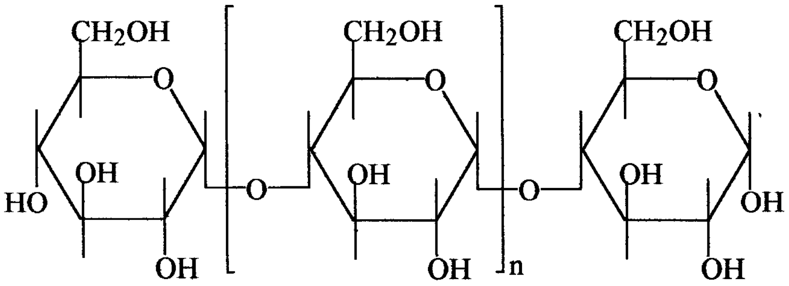


Fig. 2.1 Structure of the linear component of amylose

Amylopectin is a much larger and more complex substance. The molecule is highly branched and may contain up to 10^5 glucose residues. Amylopectin consists of α(1→4)-linked glucose chains of about twenty residues that are linked together via α(1→6) bonds (Fig 2.2). It is likely that the branches of amylopectin are not distributed randomly along the axis of the molecule but occur in discrete clusters in a region of 7-10 nm in length, which are separated by less-branched regions. The amylopectin molecules are radially arranged within the starch granule and are packed together to produce a structure of alternating crystalline and amorphous lamellae. Amylose molecules probably exist as single, randomly organised helices in the amorphous phase within the starch granule.

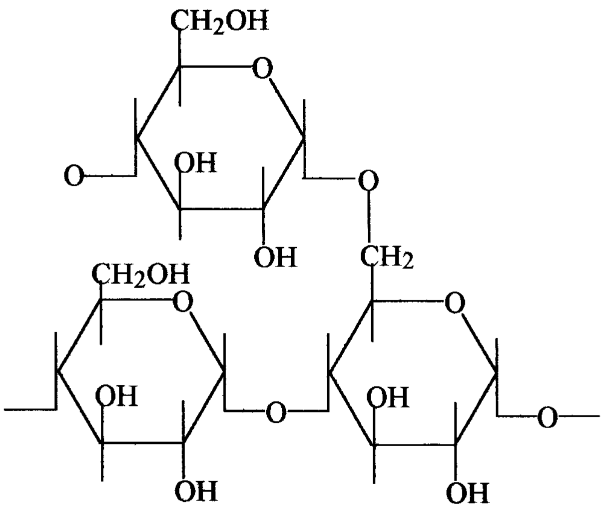


Fig. 2.2 Structure of amylopectin

There is appreciable variation in starches from different sources. This variation is apparent in the precise ratio of amylose to amylopectin. The amylose content of starch from wheat endosperm may vary from 17 to 29%, that from maize from 20-30%, and starch from potatoes may vary from 18 to 23% amylose. Starches also vary widely in the precise structure of amylopectin. In such a large molecule the potential for variation is enormous, particularly in respect of precise chain length and the degree of branching.

2.2.2 Minor constituents

Although biochemically starch can be defined in terms of its empirical formula, in industry the term "starch" is used to refer to a substance occurring as granules, containing a number of minor "non-starch" constituents such as proteins, lipids and phosphorus, which can greatly affect the suitability of starches in industrial applications. Some of these constituents are loosely associated with the surface of the starch granule, some are integrated into the starch granule or are covalently bound to the starch molecules. The occurrence of minor constituents varies between different species, between varieties of the same species, and can be influenced by growing conditions, for example, phosphorus fertiliser has been found to influence the phosphorus content of potato starch (Gracza, 1965). Some of these minor constituents, which are known to be commercially important, are described in greater detail in Chapter 3.

2.3 Pathway of starch synthesis

The synthesis of starch involves the formation of $\alpha(1\rightarrow4)$ glucopyranose chains, their extension to give amylose, their branching to give amylopectin, together with the correct positioning of the amylose and amylopectin to give the final granule. The sole precursor of starch is the sugar nucleotide adenosinediphosphoglucose (ADPGlc). This is made from the plant's central pool of C-6 sugars by the enzyme ADPGlc pyrophosphorylase, which catalyses:

$$\text{Glucose 1-phosphate} + \text{ATP} \longrightarrow \text{ADPGlc} + \text{PP}_1$$

The pyrophosphate (PP_1) produced in this reaction is hydrolysed immediately by a pyrophosphatase:

$$\text{PP}_1 + \text{H}_2\text{O} \longrightarrow \text{P}_1 + \text{P}_1$$

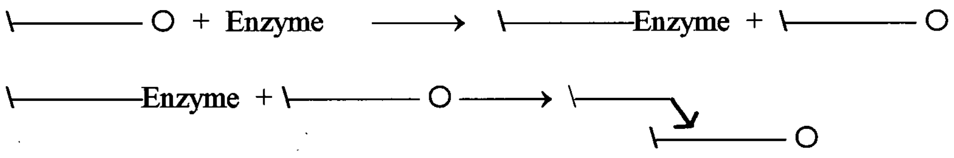
The latter reaction is strongly exergonic and ensures that the synthesis of ADPGlc is essentially irreversible. Proof that ADPGlc, produced as shown above, is the sole precursor of starch is provided by work with mutants and transgenic plants. Mutants of *Arabidopsis thaliana* that specifically lack ADPGlc pyrophosphorylase are incapable of synthesising starch. The same is true of potatoes that have been genetically engineered so as to prevent the synthesis of ADPGlc pyrophosphorylase.

ADPGlc is used to manufacture the $\alpha(1\rightarrow4)$ chains of starch. The reaction is mediated by the enzyme starch synthase, which catalyses the transfer of the glucosyl group from ADPGlc to the non-reducing end of an existing $\alpha(1\rightarrow4)$ glucan chain. The latter is called the primer; amylopectin, amylose and $\alpha(1\rightarrow4)$ glucans as small as maltose can act as primers. The transfer of the glucosyl group from ADPGlc to the primer extends the latter by one glucosyl residue but still leaves a free non-reducing end to which successive glucosyl groups may be added:

$$\text{ADPGlc} + \alpha(1\rightarrow4)\ \text{glucan}_n \quad\longrightarrow\quad \text{ADP}\ \ \alpha(1\rightarrow4)\ \text{glucan}_{n+1}$$

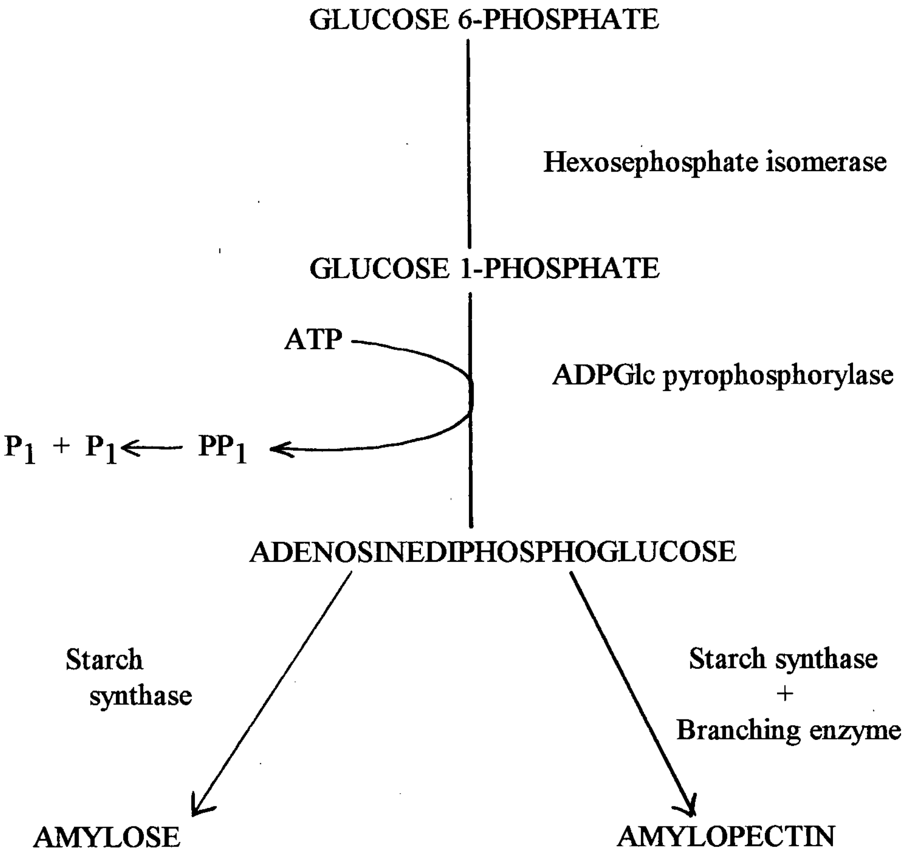
In any one tissue there are a number of different forms of starch synthase. Some of these are free and soluble, others are firmly bound to the starch granule. The extent of this multiplicity of starch synthases, and the precise roles of each form of the enzyme, are not yet known but these factors are likely to form a major part of the mechanism responsible for the organisation of amylose and amylopectin into the mature starch granule and hence are important in influencing the precise potential industrial use for the starch. For example, we already know that the major granule-bound form of starch synthase in potatoes is responsible for the synthesis of amylose.

The formation of the $\alpha(1\rightarrow6)$ branches in starch is catalysed by the branching enzyme. This process involves the cleavage of the 15-20 terminal residues from the non-reducing end of an $\alpha(1\rightarrow4)$ glucan chain, followed by the transfer of this piece into an $\alpha(1\rightarrow6)$ linkage with either the remainder of the original molecule, or another $\alpha(1\rightarrow4)$-linked glucan:



As with starch synthase, there are multiple forms of branching enzyme in any one tissue. Their precise roles are not established.

Thus the pathway of starch synthesis may be summarised as:



The amounts and types of starch synthesised in any particular cell will be determined by the availability of the initial substrate, glucose 6-phosphate, which is ultimately derived from photosynthesis, and by the relative activities of the different enzymes responsible for the conversion of this glucose phosphate to starch. The relative importance of these different factors in controlling starch synthesis is not yet established but it is the focus of considerable research at present. In most crop plants grown under favourable conditions there is likely to be ample substrate for starch synthesis and the question to be faced is: what controls the amount and type of starch that is made? From a knowledge of such control, we are likely to be able to create new varieties of crops in which the quality and quantity of starch is altered to industry's specific needs.

2.4 Conclusions

Starches vary in terms of granule size and shape, amylose and amylopectin ratio and occurrence of minor constituents. Variation occurs between species, between varieties, between different parts of the same plant and can be influenced by growing conditions. The functional properties of the starch therefore arise from the interaction of these characteristics.

Further work is required on the precise roles of each form of starch synthase. These enzymes are likely to be largely responsible for the organisation of amylose and amylopectin within the mature starch granule and hence are important in influencing the potential end use of the starch produced. Correspondingly, more work is required to elucidate the relative importance and influence of these enzymes responsible for controlling overall starch synthesis, the amount and type of starch that is made. A better understanding of starch synthesis may allow the variability of starch synthesis to be exploited commercially.

CHAPTER 3 SOURCES OF STARCHES AND THEIR CHARACTERISTICS

This chapter identifies: the main crops currently used by the starch industry, starch producing crops currently grown in the UK for food or animal feed but not extensively exploited by the industrial starch industry, and "new" starch crops, not currently grown in the UK which may have potential for the future. The characteristics of starch from different crops are described and related to industrial markets for starch. The potential for modification of starch qualities through management techniques and genetic modification is discussed.

3.1 Crops for starch production

Despite the widespread distribution of starch in the plant kingdom, most of the starch processed by industry comes from a relatively small number of crops. The most important crops for commercial starch production **world wide** are currently maize, potato, wheat and tapioca (Table 3.1) and smaller quantities of starch are obtained from rice, sorghum, waxy sorghum, waxy rice, sweet potato, arrowroot, sago, mung beans (cited in Swinkels, 1992), and tapioca (Spelman, 1994). Maize, wheat and potato starches are used for both food and non-food applications while starches from some other commercial crops such as tapioca and sorghum tend to be used exclusively for the food sector (Spelman, 1994), although any shifts to greater non-food uses in the rest of the world, especially the more tropical regions, might alter this situation.

Table 3.1 Production of major crop starches (adapted from Swinkels, 1992)

	quantity of starch processed (million tonnes/year)					
	potato	maize	wheat	tapioca	waxy maize	total
world	2.3	19.9	1.3	1.8	0.34	25.6
EU	1.4	3.4	1.2	0	0.04	6.04

In Europe, the major sources of starch are **maize, potatoes** and **wheat**. Maize is used as the source for 56% of total European starch production, (i.e. food and non-food) but there has been increasing interest in wheat starch. Total **wheat** (i.e. food and non-food) starch production has increased by 15% per annum since 1983, to take approximately 23% of the total EU market and is now produced in similar quantities to potato starch (Leygue,1993). This increased use of wheat starch has been attributed to greater demand for its co-product gluten to strengthen bread flours, a better assurance of starch supply in the long term by EU wheat (Leygue, 1993) and availability at a competitive price. However, for industrial starch use within the EU, maize accounts for 55% of the total, potato 32%, and wheat 14% (Table 1.2) i.e. although wheat and potato starch are produced in similar quantities, more potato starch than wheat starch is used in industrial markets.

Within the UK, total non-food starch use in 1993/94 was 216 221 t. Maize starch accounted for 57% of this, potato starch accounted for 30% and wheat starch 12%. None of the maize and potato starch used by UK industry is produced from domestically grown crops. Although forage maize has become popular in recent years for whole-crop silage production in the UK as far North as southern Scotland, maize is not widely grown for grain production, as existing varieties are not suitable for UK conditions. The popularity of forage maize in the UK is the result of progress in breeding early maturing varieties, and genetic manipulation may bring greater cold tolerance into starch varieties, allowing wider cultivation in the future. Although potatoes are widely grown in the UK, the special high starch varieties used by the starch industry are not grown. This is **not** due to climatic restrictions; they are not grown because there is no potato starch processing facility in the UK and therefore no UK market for starch potatoes.

In Sweden and Finland relatively small quantities of **oats** and **barley** are used by the starch industry to produce starch for industrial use. The Finnish company Rasio use 20 000 - 30 000 tonnes of barley starch for the production of starch products used in paper manufacture. These crops are widely grown in the UK for food and animal feed markets, but are not processed by the UK starch industry for industrial use. Other starch-producing crops currently grown in the UK on a small scale are **rye** and **triticale**. Although these crops are not grown in the UK for industrial starch production, it has been reported that there is an industrial use for rye starch in manufacture of adhesives, because the starch has strong water binding properties. However, it is not clear to which of the adhesive sectors (see Section 7.6) rye stock would be most useful.

Two crops which have been receiving much publicity as **"new" crops** suitable for starch production are **quinoa** and **amaranth**. Preliminary work has indicated that quinoa, which originated from South America, may be suitable for UK conditions. Yields of up to 5.1 t/ha have been obtained in experimental plots in Britain, and in Denmark, experimental yields of 3.4 - 4.1 t/ha have been obtained. Quinoa may be well suited for development as an industrial crop on set-aside as it requires relatively low inputs of nitrogen. Starch industry interest in this crop is indicated by the involvement of the large processing company "Avebe" in an EU project on quinoa. A potential limitation to the utilisation of this crop is the presence of a class of anti-nutritional compounds called saponins in the pericarp of the grain. This may restrict the use of the by-product as animal feed. However, these compounds may have uses in their own right as foaming agents or molluscicides, or as raw materials for the chemical or pharmaceutical industries.

Like quinoa, amaranth originates from South America, but domestication is less advanced. Optimum soil temperatures for seedling emergence are in the range 18.5-24°C (Webb *et al,* 1987). This obviously limits potential for the UK.

3.2 Properties of starches

Industrial starch use can be divided loosely into three categories:

(i) uses which require specific physical characteristics of the granule
(ii) uses which require specific properties of the starch solution or paste
(iii) uses for which starch is used to obtain sugar units, for example the production of surfactants (see Section 7.2.1).

Where starch is used as a source of sugar units, it may be expected that variation between sources of starch is much less important than in the other markets, and cost will be the most important factor for choice of raw material.

Some of the major factors which influence the industrial performance of starch in the first 2 categories are granule shape and size, composition of starch granules, gelatinisation characteristics, paste properties and film properties. The phenomena of gelatinisation, pasting and retrogradation are described in **Appendix 1**. Starches from different sources vary with respect to these factors. The greatest differences are found between different crop species, but variation can also be found between different varieties and as a result of management or climatic factors. It should be noted that the characteristics described here are those of **native** starches (i.e. unmodified) and in practice native starches are rarely used by industry. Starch is modified by physical or chemical treatments to improve its suitability for various industries.

The differences in starch characteristics between different crops and examples of their industrial importance are described in Sections 3.2.1 - 3.2.6. The potential for alteration of the qualities of native starches through

(i) genetic manipulation
(ii) exploitation of varietal differences
(iii) the effect of climate and management factors

are discussed in section 3.3.

3.2.1 Granule shape and size

3.2.1.1 Variation in granule shape and size. The variation between crops with respect to starch granule shape and size is illustrated in Table 3.2. The figures quoted in the table come from different sources which have described granule size in different ways. Some authors have presented average or typical granule size, while others have given a range. In addition it should be noted that descriptions of starch granule shape and size vary between authors. This may be a reflection of natural variation between samples (e.g. it may be due to variation between varieties). Although starch granules are 3 dimensional, 2 dimensional terms such as "round" are commonly used to describe them. This is due to the limitations of observation by conventional light microscopy - for example, an object which appears round may be spherical, lenticular or columnar in shape.

Table 3.2 Granule shape and size of crop starches

source	granule shape	granule size (μm)
wheat	lenticular or round (1)	0.5 - 45(1)
potato	varies widely - the largest are often egg-shaped, the smallest may be spherical, the majority are flattened ellipsoids (2)	5 - 100 (1)
maize	ranges from polygonal to rounded (1) or spherical (2)	2 - 30 (1)
barley	bulb-shaped, round or elliptical (2)	20-35 2 -6 (2)
oats	polyhedral (3)	3-10 (3)
rye	round, lenticular (3) or spheroidal (2)	28 (3)
triticale	round (3)	19 (3)
waxy maize	round, polygonal (1)	2 - 30 (1)
quinoa		1 -2 μm (5)
amaranth	round or dodecahederal (4)	1 - 3 μm (4)

(1) Swinkels (1992); (2) Moss (1976); (3) Lineback (1984); (4) Williams and Brenner (1995); (5) Fleming & Galwey (1995).

Starch obtained from **wheat, barley or rye** can be separated into different classes based on granule size, of which there are at least two. The large granules (> 10 μm, usually 20 - 45 μ m) are referred to as A type granules while small granules (< 10 μm, usually 2 - 6 μm) are referred to as B types; C and D granules refer to progressively smaller granules. Small wheat starch granules can sometimes be less than 0.5 μm.

The larger granules in wheat starch only represent about 20% of the total number of granules but account for about 90% of the weight. The A-granules have a higher value than the B-type granules which can be regarded as a by-product of A-starch production. In wheat the B-type granules have more protein associated with them than the A-type granules. High protein levels are considered a disadvantage by many industrial users. B-starch is often sold for use as animal feed, or may be used to provide a lower cost feedstock for the production of products like bioethanol where starch is used as a nutrient feedstock for bacteria or yeasts.

Potato starch granules have a wide size distribution (although potato starch is not catagorised as A and B types) which includes some very large granules - the largest of the commercially available sources. In contrast **oat** starch has much smaller granules than other UK grown cereals and the range of sizes is small. The granules are in the same size-range as rice starch, but their shape is less angular thus offering specific industrial opportunities. "New" crops quinoa and amaranth have granules even smaller than oat starch.

3.2.1.2 Examples of industrial use based on granule shape and size.

- A small amount of native wheat starch is used in paper coating (see Section 7.1) due to its granule size.
- Although oat starch is not widely processed for industrial use (it is important within the EU only in Sweden and Finland), it has been suggested that the flow and viscosity properties of the small starch granules can be technically exploited. Because of their very low granule size, which favours surface coating applications in paper manufacture, oat starch granules could be particularly suitable for the production of graphics papers since an improved printability with a less glossy surface of the paper could be achieved.
- Another use for oat starch has been developed recently by a Canadian company, Canamino. When the starch is surface-treated using the company's own technology, the oat starch flows and feels like talcum powder and can be used where the safety of talcum powder has been questioned. The "new" crops quinoa and amaranth also have very small granules which fall within a very narrow range and, like oat starch, quinoa is being considered for use in paper coating and the production of dusting powders and cosmetics (Fleming and Galwey, 1995).
- Granule size is an important factor in selecting a suitable starch type for use as a filler in the production of "loaded" plastic products (see section 6.5.1). Small starch granules are required and research is underway on the use of quinoa in this market (Fleming and Galwey, 1995).
- Granule size may play a role in determining the viscosity of aqueous starch suspensions (see Section 3.2.3.2 for some examples of industrial importance). Differences in viscosity between large-grained and small-grained starches may be caused by the larger specific surface area of the smaller granules. Water molecules

attached to the surface of starch granules result in the break-up of hydrogen bonds between the starch molecules. The smaller granules will have proportionately more water molecules attached to their surface, thus increasing the swelling power of the starch suspension.

3.2.2 Amylose and amylopectin

3.2.2.1 Variation in composition. Variation in amylose content is given in Table 3.3.

Table 3.3 Variation in amylose content of crop starches

source	amylose (%)
wheat	27 (1)
potato	22 (1)
maize	27 (1)
barley	22 (3)
oats	23-24 (3)
rye	27 (3)
triticale	23-24 (3)
waxy maize	1 (1)
quinoa	11 (3)
amaranth	7.2 (4)

(1)Swinkels (1992); (2)Lineback (1984); (3)Fleming & Galwey (1995);
(4)Williams & Brenner (1995).

The ratio of amylose to amylopectin influences characteristics of the starch such as swelling and water-binding capacities and the resulting viscosity of starch pastes. Amylose has poor stability and undergoes retrogradation (see Appendix 1) in solution. Therefore starch with a relatively low amylose content, for example, potato starch, has less tendency to retrogradation than starches with higher amylose contents. However, the **quantity** of amylose present in the starch is not the only factor influencing stability of solution; the **length** of the amylose molecules is also important. Wheat and maize starch have a high rate of retrogradation in comparison to other commercial starches e.g. potato, tapioca and waxy maize. This is likely to be due to a combination of factors including short amylose chain length and relatively high amylose content.

The "new" crops **amaranth** and **quinoa** both have a very low amylose content and are therefore likely to have a very low rate of retrogradation. Research has shown that quinoa starch performs well as a thickening agent, but poorly in cake and bread making (Fleming and Galwey, 1995). This is a reflection of the characteristics of amylopectin. It is stable in solution, but the gas retention capacity is poor and structural bonding of the granules is weak. These characteristics are also relevant to industrial uses. For example in addition to breadmaking, low amylose high amylopectin starch is not suitable for the production of thermoplastics or foam packaging materials (see Section 7.5.1).

Barley varieties exist with a range of amylose and amylopectin contents, including 100% amylopectin and high % amylose, enabling the manufacture of a range of barley starches with different **gelatinisation** properties (see below) (Munck, 1981). Barley starch processing is considered to be easier than wheat starch processing because it does not have the problems associated with gluten separation which occur in wet milling of wheat. However, without the valuable gluten by-product it is less likely to be commercially viable than wheat (see Chapter 5), unless varieties can be identified with specific high-value properties.

3.2.2.2 Examples of industrial use based on amylose and amylopectin content.

- Where starch is used as a **thickening agent** and requires **stability of solution**, in applications such as **adhesives**, the **paper** industry (and **food**), starch **high in amylopectin** and **low in amylose** is preferable. Work has shown that quinoa starch, which is very low in amylose, performs well as a thickening agent. Interest in high amylopectin starch to date has mainly come from the food industry, rather than non-food markets (90% of waxy maize starch is used in the food industry), although some use in the paper industry was recorded (Table 7.1).

- Starch **high in amylose** has good film-forming qualities and is preferred for textiles sizing (see Section 7.4.4).

- **High amylose** starch is preferred for the production of starch-based thermoplastics and packaging foams (see Section 7.5.4).

3.2.3 Phosphorus

3.2.3.1 Variation in phosphorus content. Variation in the phosphorus content of starches is given in Table 3.4. All starch from the major commercial sources contains some phosphorus but potato starch contains a higher level of phosphorus than the other major commercial sources of starch and is unique in that phosphate groups are covalently bound to the amylopectin molecules (and therefore termed "**bound phosphorus**"). The number of phosphate groups in potato starch amylopectin ranges from one to 2 phosphate groups per 400 glucose units. This corresponds to a degree of substitution (DS) in potato starch of about 0.003. The presence of the phosphate groups has important effects on the characteristics of potato starch (cited in Swinkels, 1992). For example, the low pasting temperature (see Appendix 1) of potato starch has been attributed to the presence of phosphate groups (Table 3.4) and influences industrial use (see Section 3.2.3.2).

Table 3.4 Variation in the phosphorus content of crop starches

source	phosphorus (% D.M)
wheat	0.06 (1)
potato	0.08 (1)
maize	0.02 (1)
barley	0.03 (2)
waxy maize	0.01 (1)

(1)Swinkels 1992; (2)Gracza (1965).

Table 3.5 Gelatinisation characteristics of starches

source	gelatinisation temperature (°C)	pasting temperature (°C)
wheat	58-64 (2)	80-85 (1)
potato	59-68 (2)	60-65 (1)
maize	62-72 (2)	75-80 (1)
barley	51-60 (2)	
oats	53-59 (2)	
rye	57-70 (2)	
triticale	55-62 (2)	
waxy maize	63 - 72 (2)	65 - 70 (1)

(1)Swinkels (1992); (2)Lineback (1984)

If divalent cations such as calcium and magnesium are present in the solution they may repress the swelling of potato starch granules by forming bridges between two phosphoric acid groups of amylopectin. Consequently the peak viscosity of potato starch with calcium and/or magnesium ions present is much lower than the peak viscosity of potato starch when monovalent sodium and/or potassium are present in solution (see Section 3.2.3.2).

The presence of the phosphate groups gives potato starch a **net negative charge**. Although the charge is not high, in aqueous solutions/suspensions (see Appendix 1) the repulsion of like charges may contribute to the following properties of potato starch (Galliard & Bowler 1987):

low pasting temperature
rapid hydration and swelling at relatively low temperatures
high water binding ability
high viscosity of potato starch pastes
high clarity of potato starch pastes and potato starch films.

Wheat and maize starch pastes are cloudier with a lower viscosity than potato starch pastes.

3.2.3.2 Examples of industrial use based on phosphorus content.

- Viscosity is an important property for drilling muds, wallpaper pastes, bag adhesives, wet-end addition in paper manufacture, and is also a very important property in the food industry.

- Clarity of starch pastes is an important property in the food industry. The high clarity of potato starch films is favourable for the manufacture of gummed papers (stamps, labels, envelope flaps) and gummed tape, sized yarns, and sized papers. Starches from other sources such as tapioca and waxy maize also share this property.

- A low pasting (and gelatinisation) temperature and quick speed of pasting (and gelatinisation) is an important property for fibreboard production as this allows starch to spread evenly over the entire board giving a uniform strength throughout the board.

3.2.4 Lipids

Variation in the content of lipids in starches is shown in Table 3.6

Table 3.6 Lipid content of starches

source	lipids (% D.M.)
wheat	0.9 (1)
potato	0.1 (1)
maize	0.8 (1)
waxy maize	0.2 (1)

(1)Swinkels (1992).

The **lipid** content of wheat and maize starch granules (0.8 - 0.9% of d.m.) is relatively high compared to potato. The relatively high lipid content of wheat and maize starch has the following negative effects relating to industial use.

Lipids, being hydrophobic, repress the swelling and solubilization of maize and wheat starch granules. The presence of lipids increases the pasting temperature and reduces the water binding ability of these starches.

The lipid molecules may form a complex with amylose. The presence or formation of insoluble amylose-lipid complexes causes turbidity and precipitation in starch pastes and solutions. The amylose lipid inclusion compounds make starch pastes and starch films opaque or cloudy. In addition, this complex does not contribute to the thickening power or binding force of the gelatinised starch, thus reducing the efficacy of the product.

3.2.5 Nitrogenous substances

The term "nitrogenous substances" refers to the proteins, peptides, amides, amino acids, nucleic acids and enzymes that may be present in starch granules. The level of nitrogenous substances present in starch granules is determined as for crude protein by measuring total N and multiplying by a factor of 6.25.

The nitrogenous substances content of crop starches is indicated in Table 3.7.

Table 3.7 Variation in nitrogenous substances content of starch granules

source	**nitrogenous substances (% D.M.)**
wheat	0.4 (1)
potato	0.1 (1)
maize	0.35 (1)
barley	0.18 (2)
waxy maize	0.25 (1)

(1) Swinkels (1992); (2)Gracza (1965).

Potato starch contains a lower level of **nitrogenous substances** than wheat, maize or barley starch. Proteins are associated with starch granules where they can be either integral components of the granule, or present on the surface. The high levels of proteins found in cereal starches can have some undesirable effects such as a mealy flavour and odour in pre-gelatinised starches, a tendency towards increased foam formation in cooked pastes and colour formation in starch hydrolysates.

Paper manufacturers dislike the high protein content of wheat starch. Many paper manufacturers prefer potato starch because it is "cleaner".

3.3 Potential for breeding, genetic engineering and management of crops for specific starch qualities

3.3.1 Exploitation of inherent variation

Work has shown that variation exists in starch characteristics as a result of varietal differences, agronomic practice and growth location. A number of examples are cited by Gracza (1965). Table 3.8 shows the results from some early work which found differences in phosphorus, nitrogen-containing compounds and fatty acid content between winter and spring wheat. In addition in wheat, granule size and number may be related to cultivar (Dengate and Meredith, 1984).

Table 3.8 Characteristics of starch from winter and spring wheat

	hard red spring wheat	**hard red winter wheat**
% phophorus	0.070	0.059
% nitrogen-containing compounds	0.25	0.27
% fatty acids	0.56	0.51

Source: Gracza (1965).

Varietal differences of this kind are likely to interact with environmental factors to determine the characteristics of starch from specific crops. Differences between starch produced by different factories or sourced from different regions have been noted by some starch manufacturers, but at present these differences are not commercially exploited. For example, wheat from the North and South of France has different characteristics but all goes into the same silo for processing to produce a starch blend of different regions and varieties. The final qualities of the starch are likely to be inflenced by a number of factors. One starch manufacturer has stated that some buyers only want starch from a particular factory. This preference is likely to be due to "trial and error" rather than a knowledge of why the preffered starch varies from starch produced by other factories. No detailed and definitive data are available on the effect of climate and geographic location on the development of starch granules and the properties of the extracted starches. However, some examples of differences which have been recorded are listed below.

- Phosphorus fertiliser has been found to increase the phosphorus content and paste viscosity of potato starch. Gericke (1959, quoted in Gracza, 1965) found that the average increase of the starch content in potatoes due to fertiliser was 0.8 - 1.0%. Wegner and Koepf (1963, quoted in Gracza, 1965) however, stated that fertilisers have only a minor influence on the yield and the phosphorus content of potato starch and that growth locations and weather conditions have a larger effect.

- Temperature effects have been studied in developing barley grains (MacLeod and Duffus, 1988). Elevated temperatures cause a decrease in the grain dry matter due to a reduction in the volume available for starch accumulation and the number of starch granules deposited. Although their numbers were reduced at elevated temperatures, the size of the A-type granules was slightly increased.

- With regard to potatoes, the genotype had an effect on the properties of the starch granules (Cottrell *et al*, 1995). The growing conditions affected starch granule characteristics, with starch from cultivars growing in a heated glasshouse having higher gelatinisation temperatures and amylose contents as well as being more resistant to degradation by α-amylase.

A clearer understanding of the relationship between environment, variety, agronomic practice and starch quality may enable the natural variations in starch properties to be exploited. Starch extracted from crops grown in different locations or from different varieties may be particularly suited to certain industries. However, the extent to which this variation can be exploited will depend on the consistency of environmental effects and, like some genetic modifications (see Section 3.2.2), the value of the 'speciality' starch relative to the cost of processing small batches.

3.3.2 Genetic modifications of crops

Genetic modification of plants offers an approach for the creation of novel starches more suited to particular industrial uses. For example, it may be possible to modify the plants so that they produce a starch with new functional properties similar or superior to those achieved by post-harvest modification of the starches, but retaining the important characteristics of the native starch.

The extent to which genetic modification of starch for industrial uses will be economic is difficult to assess. In general, the amount of any "new" starch required would have to equal the daily capacity of a primary processing plant. For example, the amount of starch processed in one day at the Cerestar factory in Manchester is 1800 t. Small quantities of specific starches (i.e. less than 1000 t) could not be processed economically because of the down-time between batches. A practical solution might be to sub-group the modifications so that the plant could produce a "part-modified" starch that could be subsequently processed for a range of different products. However, if a product of sufficiently high value is obtained, it might be economically feasible to construct a smaller processing factory to cope with such "designer" batches.

The public attitude towards genetic modification of plants is varied and the range of opinions within the population also differs from country to country. It is important to define what the term "genetic modification" means. Too often, genetic modification is considered to be synonymous with genetic engineering and that raises all the ethical questions associated with the subject. In the widest sense, genetic modification must include all the breeding strategies since they manipulate the genetic profile of the plant. The public has accepted this form of genetic modification since breeding strategies were first introduced. These breeding strategies have increased yields of crops, removed or lowered the levels of toxic constituents or conferred increased resistance to pests and diseases. Without selective breeding, or genetic modification, agriculture throughout the world would not have advanced to its current position.

Natural genetic modifications have resulted in starches being produced which have very different compositions and properties than the wild type. The criterion of acceptability relates to the fact that the modification can only cause changes to the existing product characteristics and properties. They cannot make the plant produce entirely new products. Maize is the cereal which has been investigated to the greatest extent and a number of mutants have been identified and classified. As an example, it has been found that the ***waxy*** (or ***wx***) mutant has a locus on chromosome 9. The starch granules isolated from maize with the *wx* allele contain about 25% amylose and 75% amylopectin. Mutants which contain only the *wx* locus contain no amylose: the starch granule contains amylopectin as the sole polysaccharide present. Therefore, if a particular application requires pure amylopectin, a direct source is available. When starches are used in existing industrial applications, those with a high amylopectin content are more stable during ageing. A further benefit of producing amylopectin by this route rather than from a typical starch granule is that the economic and environmental costs of separating the amylose component from the amylopectin are absent.

Another example of a genetic modification, also first found in maize, is the ***sugary***, or ***su***, mutant. This mutation does not produce what is generally accepted as amylopectin. The amylopectin is replaced by a more highly branched polymer which also has much shorter side chains. The polymer is still only composed of glucose residues in the same bonding arrangement as amylopectin, but it is a water-soluble polysaccharide, and therefore considered as distinct from amylopectin. It is present at up to 25% of the kernel weight. The polysaccharide has been named phytoglycogen, due (see Appendix 2) to its close similarity in chain length to animal glycogen.

While the biochemical reasons for the formation of phytoglycogen have not been fully resolved, it has been known for some time that the absence of amylose in the ***waxy*** mutant is due to the absence of the enzyme granule-bound starch synthase 1 (GBSS1). Hence, the retention of this natural mutation has resulted in a series of cultivars of maize which produce no amylose, and the waxy maizes are commercial products.

The waxy mutation has also been found in barley. It is also caused by a single gene mutation but there is a difference from maize in that the change has been mapped to chromosome 1. The barley mutation does seem to show some difference from maize in that the presence of amylose is not entirely eliminated. Another mutation in barley, which could be of commercial benefit, was found in the cultivar Glacier. This mutant produces a starch which has about 45% amylose (i.e. almost twice the normal level), and should be a suitable candidate for applications requiring either a starch with a higher than normal amylose content or any future industrial use of pure amylose. For the second type of application, a separation step would still be necessary to remove the amylopectin, but more cost-effective than using a conventional cultivar. To date, these mutants have not been fully exploited for industrial uses but do find applications where a high amylose content gives a superior starch film than conventional starches. While amylose-free mutants are available, there are no reports of amylopectin-free starches and, from the nature of the starch granule, it is unlikely that such a mutant could occur.

Mutations capable of producing starch granules with such wide variations in composition have not been reported for wheat. This is primarily due to most wheat varieties being hexaploid while barley is a diploid species. The higher the ploidy, the lower is the ability to establish a particular genetic trait.

Most cultivated potato species are tetraploids and the range of mutations exhibited by maize and barley (diploids) has not been found. Nevertheless, an amylose-free mutant has been found in potatoes. Since waxy has an existing connotation in relation to potato quality, the mutation has not been designated in the same way but the mutation has been shown to be similar to that in ***waxy*** maize since it lacks the enzyme GBSS1. Commercial production of this mutant has now taken place and the starch will have an outlet in applications requiring good long-term stiffness.

There are many of these outlets but the ones of major economic importance are for coated papers and as adhesives for board and packaging materials. Potato starch is still the preferred starch for the paper industry due to its lower lipid and higher bound phosphate content. Like all starches from conventional sources, potato starch is still not ideal since its viscosity must be lowered and made more stable. This is due to the amylose component which changes its conformation during storage and aging. The high amylopectin or amylose-free starches are less viscous and more stable than their conventional counterparts.

Only when these amylose-free mutants are fully available for commercial exploitation can the economic costs of genetic modification be compared with the costs of chemical modification. However, it should be noted (Table 1.2) that the production of chemically modified starches as ethers and esters is the second largest industrial starch market in the EU. In contrast (Table 1.1), it is a relatively minor market of the UK starch industry. Many of the starch ether and ester markets could be filled by amylose-free starch products. The environmental costs and benefits should be in favour of the genetically modified material since many of the chemicals used to modify are toxic or carcinogenic.

3.3.3 Genetic engineering

This aspect of genetic modification raises ethical issues which will not be discussed in this report. Nevertheless, it is suggested that genetically engineered crops whose products are used for non-food (i.e. industrial) uses are likely to be accepted by a higher proportion of the population. Avebe consider that genetic engineering is acceptable to the general public in the Netherlands and do not seem to expect that they will face legislative problems from the use of genetically engineered plants. Some producers, however, have been asked by end-users for certificates to confirm that starch products have not been produced from genetically engineered plants.

Progress with the introduction of genetically engineered crops has, so far, been easier in the UK than the rest of Europe. The major genetically engineered crop is oilseed rape, and marketing consent for herbicide resistant rape was recently granted in the UK although it has still not been cleared at the European level. It must be recognised that opposition to genetically engineered crops is high in some European countries which will make it difficult to predict the contribution which can be made from altering starch-producing crops.

Genetic engineering can be used in 2 ways to alter the characteristics and properties of the plant products. In the first way, alteration of a gene or genes can be used to enhance or eliminate an existing plant constituent. As an example, an antisense gene which is able to suppress the expression of the gene for the GBSS enzyme has been introduced into the potato. Stable and total inhibition could be obtained, with considerable reductions in amylose contents compared with the wild type. The typical value for potato starch of 22% amylose is reduced to essentially amylose-free. The genetically altered cultivar is currently under trial, and Dutch farmers are due to grow about 600 ha in 1996 for more intensive testing by Avebe.

After the 1996 trials, the potential of this amylose-free potato should be clearer and a decision will be taken on the future of the variety. It is hoped that the amylose-free potato starch will have comparable properties to waxy maize starch but retain some of the advantageous properties of existing potato starch, such as phosphate groups. If it can compete with waxy maize, it is hoped to take at least 10-20% of this speciality market which has a size of 40 000 t. In addition the new starch may be suited to some markets currently supplied by other conventional starch types.

It is anticipated that large scale production could be established within 6 years. However, the company is taking precautions by continuing the development of varieties with the same characteristics but using conventional breeding methods. Therefore, if objections to the use of genetically modified plants are established, it will only delay and not prevent the introduction of the amylose-free potatoes. The yield of the modified plants depends on the initial variety used. The Dutch have used a variety, Karnico, which yields 110% compared to control varieties. The amylose-free version is claimed to yield 105% of the control.

Attempts are also being made to develop high amylose potato varieties, again in The Netherlands and supported by Avebe. These developments are not as far advanced as the amylose-free varieties. The reduced impetus is related to the existing low market for amylose. High amylose starches do exert superior film-forming properties which are suited to plastics production but the quantities of starch-based plastic currently manufactured are small (see Section 7.5).

The same criterion can be applied to the phytoglycogen position. This range of polysaccharides could also have applications in the plastics industry since the more frequent branch points and shorter average chain lengths make these structures water soluble. There are obvious advantages in this phenomenon, especially in the isolation and purification of the polymers. However, until sufficient amounts of the material are produced and its actual benefits as an industrial raw material are established, its development will be slow. Since the modifications to produce phytoglycogen are caused by alterations to more than one enzymic activity, it would be possible to produce a range of phytoglycogens with different properties.

As well as altering the amylose:amylopectin ratio in the plant, genetic engineering can also be targeted to increase the yield of starch *per se*. Strategies do exist to divert the products of photosynthesis along different pathways. One such enzyme, which can alter source-sink partitioning of these products of photosynthesis, is adenosinediphosphate glucosylpyrophosphorylase (ADP-G-PP). It is reported to be the key enzyme in initiating starch biosynthesis. Expressing the gene for this enzyme in the antisense manner severely reduced the level of the enzyme which, in turn, reduced the starch levels and increased the sugar levels in the tubers. The reverse reaction should also occur if the levels of enzyme activity could be increased. The gene from a plant source has not been characterised but a similar gene has been isolated from *E.coli* and, having been transferred, does indeed lead to higher levels of starch in the tubers.

One of the features of potato starch is the small but significant level of phosphorus which is present in a bound form in the amylopectin component. Its presence is reported to be one of the reasons why potato starch is recommended and preferred for the paper industry and the oil drilling industry. The bound phosphate groups allow the starch to act as a cation exchange resin and bind to the cellulosic constituents of the fibres. Cationic starches can be produced by chemical methods and are at the high value end of starch products. Although there are no known reports in the literature of attempts to carry out this genetic transformation, it may be possible to isolate and identify the gene(s) responsible for introducing the phosphate group into the amylopectin molecule of potato starch. Once characterised, it should be a straightforward process to increase the concentration of these phosphate groups to produce a truly natural cationic starch.

The major current user of cationic starches is the paper industry. The cationic starch is manufactured by chemical transformation of cereal starches and occupies the same role that other starches do. It is claimed to be superior to unmodified starches since a far higher proportion of the added starch remains bound to the paper and is not lost in the vast amounts of water used by a paper factory. There are, therefore, environmental benefits in using a cationic starch. The introduction of a higher proportion of phosphate groups into potato starch would exhibit considerable economic and environmental benefits.

The other aspects of genetic engineering are to produce chemicals which are not native to the plant. One such group is the cyclodextrins. Cyclodextrins are a series of 6, 7 and 8-membered cyclic structures which are formed when chains of the correct number of $\alpha(1\text{->}4)$- linked glucose residues (as found in both amylose and amylopectin) link internally from head to tail. The internal link makes them far less reactive than other oligosaccharide chains while the structures are relatively stable due to the series of
$\alpha(\text{->}4)$- linkages readily adopting a helical conformation.

Cyclodextrins are occupying an increasing number of niche chemical markets. The exterior of the molecules are hydrophobic while the interiors are apolar. The physical properties are different depending on the number of glucose residues in the ring so the range of opportunities are great. The major area is their use as inclusion complexes. The formation of an inclusion complex can result in increased stability of the included compound and the targeting of water insoluble chemicals or drugs to a specific site in an aqueous environment. There are, therefore, wide ranging opportunities for using these materials in pharmaceuticals and agrochemicals.

An enzyme, cyclodextrin-glycosyl transferase, is found in several species of bacteria and catalyses the conversion of pre-formed starches into cyclodextrins. The gene for the enzyme has been identified from one of the bacterial sources and it has been transferred to potato tubers. Small but detectable levels of the cyclodextrins have been confirmed. Expression will have to be greatly increased before the yield of product is sufficient for commercial exploitation.

There are also no known reports in the literature of any of the following transformations having been attempted but the possible range is very is very wide. As reported in Chapter 6, chemically modified starches are added value products which are in demand in most of the markets outlined in Chapter 7. The potential of a cationic (high phosphate) starch has been discussed but the introduction of anionic and other cationic groups should be feasible. The primary hydroxyl group attached to C-6 of most glucose residues in the starch polysaccharides is fairly reactive and it is probably not beyond the ingenuity of the genetic engineer to attach anionic or cationic groups at these sites. An alternative approach to the insertion of "foreign" material to produce cationic or anionic starches would be to incorporate the natural acidic and basic sugar analogues of glucose, glucoronic acid and glucosamine, into the starch structures. In practise, it is likely that only the incorporation of glucosamine might be economically worth-while. A polysaccharide with high (up to 90%) concentrations of a related acidic sugar, galacturonic acid, exists naturally in abundance as pectin.

3.4 Conclusions

The potential of new starch producing crops should be assessed. In particular a watching brief should be maintained on **quinoa** which has acceptable yields under UK conditions. Similarly, detailed characterisation of starch produced from non-traditional starch crops which grow well in the UK (e.g. oats) is required with a further investigation of their industrial potential.

There is a striking need to assess the relative importance of climate, growing location and management on the potential for influencing starch quality and industrial potential. If effects were sufficiently large then this could provide a rapid and inexpensive method for producing starch of differing characteristics. Genetic modification, both by conventional and genetic engineering techniques, offers the opportunity for producing radically different starch qualities in the medium to long term. It is vital that those responsible for these developments maintain a close dialogue with starch industry processors and users in order to ensure that the varietal types being developed will cater for a sufficiently large market size.

CHAPTER 4 PRIMARY PROCESSING

This chapter describes process technology for the extraction of potato, wheat and maize starch. The processes described in this chapter are used as the basis for the economic analysis presented in Chapter 5.

4.1 Potato processing

The production of starch from potatoes is a seasonal operation. Processing is concentrated within a short season to minimise storage costs and storage losses. Potatoes are not well suited to annual storage as they have a moisture content of around 75 - 80%. The Dutch potato starch processing season or "campaign" begins in August, when potatoes are first harvested, and continues, with stored potatoes, into February. The campaign will sometimes extend into spring, but quality decreases as storage time increases. After harvest, potatoes are stored by growers either on the farm of origin or collectively in larger off-farm stores. They are collected and transported to the processing factory as required. Towards the end of the season, if starch potato supplies are short, some varieties for human consumption may be used, although their starch content at around 16% of fresh weight is low relative to the specialist starch varieties (20 - 23% of fresh weight).

Potatoes delivered to the starch processor normally have some soil and stone admixture. The first processing step is to wash the potatoes and separate out loose soil, stones and other debris. Cleaned potatoes are then pulped. The pulp is separated into a starch slurry, fibre and potato juice. The starch slurry is purified by further washing, dewatering and drying.

Some variation in the specific details of processing exists. Potato starch manufacturing technology as developed by Hovex Engineering B.V., Veendam, The Netherlands is presented here as an example of process technology currently in use. Hovex are specialists in manufacture and design of complete plants for the production of starch from potatoes and other crops. A key feature of this system is the recycling of water, thereby reducing fresh water consumption and effluent production. The high water content of the potatoes is exploited with water recycled throughout the whole process.

4.1.1 Manufacturing technology

The Hovex system involves the following 7 stages.

4.1.1.1 Storage. Potatoes are delivered to a storage pit. Hovex advise covered storage, to give a longer storage and processing season. This is, however, a more expensive option than open storage. Dirt and loose stones are removed from the potatoes prior to storage.

4.1.1.2 Washing. Potatoes are transported with water from storage through 2 sets of wash drums and stone catchers. In the second wash drum, floating debris such as leaves are separated. Washed potatoes are then transported by belt to a final rinsing belt where any remaining wash water is sprayed off by recycled process water. From here they move into a storage hopper.

4.1.1.3 Disintegration. Potatoes are fed from the storage hopper into a disintegrator where they are rasped to a fine slurry. The rasper, a rotor with 120 interchangeable cutter blades, rotates at 2000 r.p.m.. This rasping process opens up the cells which contain the starch.

4.1.1.4 Extraction. The potato slurry is pumped to an extraction line which consists of a 4-stage sieving unit. Washing takes place in a counter-current operation. Water recycled from subsequent steps is fed into the extraction station. The starch milk and fibres are separated out. Fibres move to the dewatering sieve where the moisture content will be reduced to *ca.*86%. The starch solution or "starch milk" is transported to a 5-stage hydrocyclone section. The first step removes foam from the system. Fruit juice, a fraction of this solution containing amino acids, potassium and citric acid, is clarified in the second step and starch milk is concentrated in steps 4 and 5. The starch milk is then dewatered on a horizontal belt filter and washed out with process water. This is done to remove all the fruit juice from the starch milk. Effluent is recycled and the starch milk is pumped into a starch milk tank. Before the starch milk enters the main refining line, it is desanded by a sand cyclone.

The refining of the starch milk is split into two lines: the main refining line and the fine granule line. This allows removal of all small fibres and other impurities which have the same density as fine starch.

4.1.1.5 Main refining line. Starch milk is refined with fresh water. The main refining line is a 14-stage hydrocyclone section. Before entering the refining hydrocyclones, the raw starch milk is sieved in a 2 step rotary sieve system, where small fibres are separated. The starch milk is then fed into the second step of the pre-concentration unit. The overflow of the first step refining is fed to the small granule line. The washed starch is concentrated in the last step down to 22° Baumé[1] (bé).

4.1.1.6 Fine granule line. This consists of 12 steps. Fine starch is washed and fine fibres and impurities separated. The clean starch milk is transported through a hopper tank into a rotary vacuum filter where it is dewatered to *ca.* 36-37% moisture content.

4.1.1.7 Drying. Starch is dried in a flash drier to *ca.* 20% moisture content, bagged and stored.

4.1.2 Potato starch by-products

Potato starch manufacturing suffers from the relatively low value of process by-products. Avebe are researching higher value potato starch by-product markets in order to improve the economics of potato starch manufacture. Of interest are:

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[1] Baumé = a measure of density

4.1.2.1 Fibre. Fibre pulp is produced with a moisture content of approximately 85%. At this moisture content the pulp can be used as an animal feed. Some fermentation may occur during storage, but this is not generally considered a problem. However, for longer term storage, the pulp should be dried further. The fibre could also be refined for human consumption, but this is an expensive process, and is not currently employed. Potato fibres contain high amounts of pectin. This may represent another potential by-product, as there are many applications for pectin, but it is difficult to isolate. To date, the use of potato fibre has been restricted to animal feed.

4.1.2.2 Fruit juice. Potato juice contains 8% potassium, 10% citric acid and many amino acids. It can be used directly as a fertiliser or dried for use as a protein source. Use as fertiliser gives the cheapest method of disposal but is dependent on local environmental regulations which may limit its distribution. Larger starch plants may have protein processing facilities. Potato protein could be used for animal feed or human consumption, but Dutch starch manufacturers are keen to develop higher value technical applications for the protein, for example in adhesives.

4.1.3 Process yields

The yields will be dependent on the composition of the raw material. Specialised starch potato varieties will give starch contents of up to 25% by weight. EU starch regulations governing the minimum price paid to starch potato growers indicate a range in starch contents from 13.8% to over 23% of "underwater" weight. Dutch starch yields averaged around 20% by weight through the early 1990's. Standard process yields based on a starch content of 16% are shown in Table 4.1.

Table 4.1 Proportion by weight of components of potato yield

substance	content (%)
starch	16
fibres	1.5
protein	1.4
amino acids	1
ash	1
sugar	1
water	78

Process yields from a typical starch processing plant rated at 30 t/h potatoes are shown in Table 4.2.

Table 4.2 Starch processing plant yields

	t/h	t/year (150 days @ 24 h/day)
starch @ 20% moisture	5.7	20 520
pulp @ 86% moisture	3.5	12 600

4.2 Cereal processing

Cereal grains can be conveniently dried and stored, allowing cereal starch processing to continue throughout the year. In addition to starch, processing of both wheat and maize produces important co-products of which gluten is the most useful.

4.2.1 Wheat starch processing

4.2.1.1 Product yields and qualities. The **main products** from the starch plant are gluten and 'A' starch (see section 3.2.1.1). Wheat gluten is used within the flour milling industry to fortify flour for bread making and is valued at around £650/t (1994/95). The yield of the products is dependent upon the raw material composition, and its processing characteristics, but typical outputs are:

> **Gluten yield** : 11 to 13% dry basis - depends on insoluble protein content of flour
>
> **'A ' starch yield**: 58 to 64% dry basis - depends on the starch content of wheat and on the flour milling process.

The by-products are **'B' starch** (see section 3.2.1.1), **fibre/pentosans** slurry (pentosans are polysaccharides (arabinoxylans) which are present in starchy fractions but come mainly from the rest of the endosperm and the bran), and plant effluent. The high biological oxygen demand of the effluent stream makes it unsuitable for discharge into water courses. There are several uses and disposal routes for these by-products.

B starch can be mixed with the **fibre** and **pentosans** and sold as an animal feed, either wet or dried. Disposal of this mixture in the wet form is most economic, but there will be deterioration with increasing storage time. Although this can be minimised by pH control and dosing with reagents, the dried product is preferable if storage is required. Dried B-starch and pentosan mixture may also be suitable for 'backmixing" with flour to make a de-fortified flour suitable for biscuit-making. Alternatively the B starch and pentosans can be dried separately. A major use for dried B starch in Europe is as a milk replacement for calves and pigs. B starch is also suitable for some industrial applications, e.g. for the production of wallpaper pastes or for use as a feedstock for bioethanol or citric acid production, or as a thickener for foods.

Where convenient, the **effluent** can be pumped directly from the factory to the fields for use as a fertiliser, but the amount that can be discharged in this way is limited. Another use for the effluent is as a nutrient for antibiotic manufacture.

Evaporation of the effluent is an energy intensive operation but is becoming more popular. The **evaporator syrup** contains approximately 25 - 30% dry solids and can be used as an animal feed, either wet, or dried together with fibre, pentosans and wheat bran. The final condensate from the evaporator can, in most cases, be sewered with minimal further treatment, or if necessary can be purified and re-used as fresh water in the starch process.

Some wheat starch processors install **anaerobic** effluent treatment plants, especially if there are other similar waste streams, for example waste from a glucose plant.

4.2.1.2 Processing technology. Various processes are used for the extraction of wheat starch. Barr and Murphy are an international group of process engineers specialising in grain starch separation. Details of their process are presented here as an example of process technology currently in use. The Barr and Murphy process begins with flour either from a dedicated mill or from outside sources. The process involves the following stages.

Wheat flour and water are mixed to form a **dough**. As flour and water are mixed the extraction of the vital gluten is initiated. The dough is fed into high intensity rotary homogenisers where shear forces break up the matrix and separate it into a **3 phase mixture**. This mixture is separated by Tricanters.

The first phase is the A starch which is almost pure and contains less than 1% protein. This phase is transferred from the Tricanter to a hydrocyclone refining system where it can be refined to a protein content of *ca.* 0.3%. The A fraction is washed and screened to remove fibre. In the process of fibre separation and washing the A-starch milk is concentrated by hydrocyclone to 21° bé. The starch is dried in a flash drier.

The second (heavy) phase contains the B starch and gluten which are separated by screening out the gluten.

The gluten is collected in a hopper and pumped to the gluten drier. Dried gluten is discharged through a screw conveyor and rotary valve into a discharge screw, from which some material is recycled while the rest is fed into an air classifier mill, or mill and sifting set to ensure the required product particle size.

The filtrate from the gluten screen and washer contains some 'A-minus' starch, B starch and fine fibre. The fine **fibre** is removed by screening. The starch mixture is separated into A-minus starch and B starch. The **A-minus starch** is returned to the main A starch stream and the **B-starch** is recovered in a decanter. Effluent is largely recycled back into the process to minimise fresh water consumption.

The third (light) phase contains pentosans, solubles and some fine gluten. The gluten is recovered from this stream by screening and collected in the gluten hopper. The filtrate with pentosans is clarified using a screening system. The remaining effluent, containing only solubles, is discharged as the final effluent.

4.2.2 Maize starch processing

4.2.2.1. Product yields. Maize starch is extracted using a wet milling process. By-products of the process are oil, corn gluten feed, gluten meal and germ cake. Maize starch by-products are sold principally to the animal feed market, but maize oil is used in the food industry.

100 kg of maize yields approximately

62 - 63 kg of starch
3 kg of crude oil extract from the germ
19 - 20 kg of corn gluten feed
4 - 5 kg of gluten meal
4 kg of maize germ cake

4.2.2.2 Processing technology. The wet milling process for maize starch consists of the following steps (Anon, 1986):

Steeping of grains. Grains are steeped in tanks to make them swell and soften so that the hull and germ can be separated and soluble products removed. The water from steeping, which contains the solubles (steep water) can be concentrated by evaporation to produce steep liquor. This by-product is mixed with the fibre (see below) to produce corn gluten feed and can also be used as a nutrient for the production of antibiotics.

Germ separation. Coarse grinding splits the swollen kernel to free the oil-containing germ. The germ is then separated by the use of centrifuges or hydrocyclones, washed, dried and pressed to extract crude oil. The defatted germ is sold as maize germ cake for animal feed.

Milling and sieving. Finer milling separates the fibre from starch and gluten in the endosperm. The fibre is then removed by sieving and mixed with the steep liquor as described above to produce maize corn gluten feed.

Separation of starch and gluten. Starch and gluten are separated by centrifugation. The starch slurry is then purified by a battery of hydrocyclones. It contains a maximum of 0.3% of protein. The gluten is used in the form of "gluten meal" - a flour containing more than 60% protein, which is used as an animal feed.

Maize gluten has a lower value than wheat gluten (around £80/tonne, for 1994/95).
Wheat gluten is more difficult to extract than maize gluten because it is more sensitive to heat or chemical damage.

CHAPTER 5 STARCH PRODUCTION ECONOMICS

This chapter describes the EU schemes which currently support industrial starch production and compares gross margins for maize, potato and wheat starch production.

5.1 The EU production refund and potato starch quota schemes

The extraction of native starch from cereals, potatoes and rice, within the EU, is dependent upon the payment of production refunds under the terms of the Common Agricultural Policy. These refunds, paid since 1 July 1989 only to non-food, industrial users of starch, compensate for the high internal EU price of raw materials, relative to world prices, and allow EU starch to compete with cheaper imported supplies in EU industrial markets (Council Reg. 1722/93). Industrial users are defined as those involved in the manufacture of non-annex II goods - goods not covered by the terms of the Common Agricultural Policy.

The EU food and drink starch market is in turn protected by the imposition of a system of import levies and export refunds. Import levies discriminate against imported supplies while export refunds allow EU starch manufacturers to compete on world markets.

Potato starch manufacturers are given additional support with the payment of a fixed premium per tonne of starch produced (Council Reg. 1766/92).

Table 5.1 sets out the direct support available to EU starch manufacturers in 1994/95.

Table 5.1 Direct support to EU starch manufacture 1994/95

	ECU/tonne starch maize/wheat/rice/potato	**ECU/tonne starch barley/oat**
Production refund (1)	79.2	94.23
Fixed premium potatoes only (2)	22.25	

(1) May 1995 OJ L112 Com. Reg. No. 1131/95
(2) 1994/95 OJ L16 Com. Reg. No. 97/95

Production refunds for maize, wheat, rice and potatoes are calculated monthly by applying a coefficient of 1.6 to the difference between the maize/barley intervention price for the month in question and the average maize price over the first 25 days of the preceding month. These refunds are claimed by non-food industrial users of starch manufactured within the EU and support a high internal EU starch price.

Production refunds paid on barley and oat starch are calculated separately by applying a coefficient of 2.7 to the difference between the maize/barley intervention price and the average barley c.i.f. (carriage, insurance and freight) price, calculated again over the first 25 days of the preceding month.

The distribution of barley and oat starch production refunds is restricted to the following quota allocation introduced from 1/1/95.

Finland	50 000	Sweden	10 000 tonnes (1)

(1) EC Reg. 3125/94

The potato starch "fixed premium" is allocated within an EU quota system on socio-economic grounds, with the intention of supporting established potato starch industries, and their associated farmer suppliers. The fixed premiums are paid to potato starch manufacturers who pay the minimum prescribed price to potato growers within a cultivation contract. The distribution of these premiums is limited to a maximum quantity of 1.592 million tonnes (EC Reg. 1868/94) allocated as:

	tonnes		tonnes
Germany	591 717	Denmark	178 460
Holland	538 307	Spain	2 000
France	281 516		
		Total	**1 592 000**

These quotas, calculated independently of the other EU agricultural support schemes (e.g. the arable area payment scheme) are reviewed every three years and have been allocated on the basis of production over the base period 1990/91-1992/93. An additional reserve of 110,000 tonnes has been allocated to Germany to cover an expansion in capacity within the Eastern Länder where investments were made prior to 31/1/94.

There is domestic demand for potato starch in the UK, which is currently satisfied by imported starch (see Table 1.1), and a tradition of potato-growing. UK farmers could therefore supply a new potato starch processing industry, and the potato starch produced would reduce imports. However, considering the rationale behind the allocation of the potato starch quota (i.e. to support **established** potato starch industries) and the desire of the European Commission to restrict expenditure within the potato starch regime together with the lack of any potato starch manufacturing tradition in the UK, it is considered unlikely the UK would ever be awarded a potato starch quota that allowed the payment of 'Fixed Premiums' to UK manufacturers. This will discourage the establishment of a UK potato starch industry.

5.2 Processing margins

Typical 1994/95 processing margins achieved by the wheat, potato and maize starch industry were calculated as:

wheat starch	£56.00/t of starch
maize starch	£53.00/t of starch
potato starch	£18.00/t of starch

The processing margin is defined as the margin over direct raw material costs, capital and processing charges. It is required to cover working capital, management and marketing, leaving a return to the business. Their calculation is fully explained below. Individual plant costs will vary in relation to their depreciation policy, the age of plant and method of working.

Wheat starch margins at £56.00/tonne are shown to be similar to, but slightly more attractive than maize starch. Production refunds paid to industrial users of wheat starch are equal to maize refunds despite a lower EU wheat procurement price, giving a small advantage to wheat starch. Some revision in the calculation of wheat starch refunds is under consideration to take into account lower raw material prices.

Potato starch margins are well below maize and wheat margins and match closely the value of the starch premium paid to potato starch manufacturers. Without this premium, given current market prices, potato starch manufacture would cease.

These calculations assume a starch value of £300.00/tonne ex factory. This may be considered low in relation to 1994/95 values which are closer to £350.00/tonne, but is considered to represent the average price level achieved by the industry over recent years.

5.3 Potato starch economics

Mass balance

1.0 tonne of potato (@ 20% starch content) yields: 0.230 tonnes starch @ 20% moisture

0.140 tonnes pulp @ 86% moisture.

processing losses may reduce yields by up to 2.5%

Source: Hovex.

Input/output values:(1994/95) trade estimates.

Starch potatoes	£45.00/t	delivered
Potato starch	£300.00/t	ex-factory
Potato pulp	£10.00/t	"

Annual capital charge £19.00/t

Assumes: plant capacity: 40 000 tonnes p.a starch 170 000 tonnes p.a. potatoes
capital cost approximately £16 m charged at 10% over 10 years
capital cost/tonne potatoes: £94.12/tonne
annual charge @ 10% over 10 years £15.34/tonne.

Processing costs: approximately £10.00/tonne potatoes
(labour, energy, maintenance).

Processing margin per tonne of potato starch

		Tonnes		(£/T)	Value (£)	
Outputs:	Starch	1.00	@	300.00	300.00	
	Pulp	0.60	@	10.00	6.00	
	Fixed EU Premium	1.00	@	18.71	18.71	
Total returns per tonne of starch (assumes no processing losses)						**324.71**
LESS						
Potato input		4.35	@	45.00	195.75	
Annual capital charge per tonne of starch				approximately	66.73	
Processing costs per tonne of starch				approximately	43.50	**305.98**
Processing margin per tonne of potato starch						**18.73**

Potato starch processing margins rely principally on the sale of potato starch. By-product values are low with direct EU support payments making an important contribution to the final margin.

5.4 Maize starch economics

Mass balance

1.0 tonne maize yields:
0.625 tonnes starch
0.195 tonnes corn feed
0.045 tonnes gluten meal
0.036 tonnes maize germ
0.024 tonnes crude germ oil

Processing losses may reduce yields by up to 2.5%

Input/output Values: (1994/95) trade estimates

Maize (French)	£140.00/t delivered
Maize starch	£300.00/t ex-factory
Corn feed	£80.00/t "
Maize gluten meal	£200.00/t "
Maize germ	£90.00/t "
Crude germ oil	£430.00/t "

Annual capital charge: approximately £40.00/tonne of maize grain capacity (SAC estimates).

Processing costs (labour, energy, maintenance, materials) approximately £12.50/tonne of maize (SAC estimates).

Processing margin per tonne of maize starch

		Tonnes		(£/T)	Value (£)	
Outputs:	Starch	1.0	@	300.00	300.00	
	Corn feed	0.312	@	80.00	25.00	
	Gluten meal	0.072	@	200.00	14.40	
	Maize germ	0.058	@	90.00	5.22	
	Crude oil	0.038	@	430.00	16.34	
Total returns per tonne of starch (assumes no processing losses)						**360.96**
LESS						
Maize input		1.6	@	140	224	
Annual capital charge per tonne of starch				approximately	64.00	
Processing costs per tonne of starch				approximately	20.00	
						308
Processing margin per tonne of maize starch						**52.96**

Maize starch by-products are sold principally into the animal feed market. Some crude maize oil will be utilised in food manufacturing. By-product values are, as a result, determined in relation to cereal and protein feed prices. By-product values, while remaining important, have much less impact on processing margins than with wheat starch manufacture; maize starch prices being the main determinant of maize starch processing margins.

5.5 Wheat starch economics

Mass balance:

1.333 tonnes whole wheat yields: 1 tonne wheat flour.

1.0 tonnes wheat flour, with the addition of wheat bran yields:	0.1186 tonnes gluten @ 8% moisture 0.625 tonnes A-starch @ 12% moisture 0.124 tonnes B-starch @ 10% moisture 0.320 tonnes dry feed @ 12% moisture

Source: Barr & Murphy

Processing losses may reduce yields by up to 2.5%

Input/output values: 1994/95 trade estimates:

Wheat	£125.00/t delivered
Wheat gluten	£650.00/t ex-factory
Wheat A-starch	£300.00/t "
Wheat B-starch	£80.00/t "
Wheat dry feed	£80.00/t "

Annual capital charge £48.90/tonne of wheat grain capacity.

Assumes:
plant capacity: 46 000 tonnes p.a. starch. 100 000 tonnes/p.a. wheat
capital cost approximately £30m charged @ 10% over 10 years (SAC estimates)
capital cost/tonne wheat @ £300/tonne
annual charge @ 10% over 10 years £48.90/tonne.

Processing costs: approximately £25/tonne of wheat (SAC estimates)
(labour, energy, maintenance, materials).

Processing margin per tonne of wheat starch

		Tonnes		(£/T)	Value (£)	
Outputs:	Starch	1.0	@	300.00	300.00	
	B-starch	0.198	@	80.00	15.87	
	Wheat feed	0.512	@	80.00	40.96	
	Gluten	0.192	@	650.00	123.50	
Total returns per tonne of starch (assumes no processing losses)						**480.33**
LESS						
Wheat input		2.132	@	125	266.60	
Annual capital charge per tonne of starch		approximately			105.00	
Processing costs per tonne of starch		approximately			53.00	
						424.60
Processing margin per tonne of wheat starch						**55.73**

Wheat starch margins are highly dependent upon sale values of the co-product wheat gluten. A budget value of £650/tonne for gluten is low in comparison with 1994 price levels which reached £1,500/tonne when EU, Australian and North American wheat quality and availability was affected by drought. Current 1995 values of £650-700/t are more representative of normal trading conditions. Any increase in milling wheat imports within GATT agreements may reduce gluten demand forcing gluten prices below £650/tonne.

5.6 Conclusions

Processing margins for wheat starch appear more favourable than for maize or potato starch. The current system of EU support for the starch processing industry does not encourage the development of new potato starch processing capacity in areas, like the UK, with no existing industry. Given the financial cost of these supports it is considered unlikely that the European Commission will allow any expansion of the quota to bring new potato capacity into production. Potato starch manufacture could only become viable without the "fixed premium" if by-product values could be improved significantly, for example to match those obtained for wheat gluten.

CHAPTER 6 SECONDARY PROCESSING

This chapter explains the need for processing native starches and describes the processes and different types of processed starches produced.

6.1 Benefits of secondary processing

Starch manufacturers add considerable value to native starch with secondary processing to give a wide range of modified starches to meet specific market requirements. Primary processors may modify up to 80% of starch production, using 5 or 6 main chemical modifications to produce around 400 different starch products. Typically, modified starch prices are more than double those of native starch and will make a significant contribution to the overall starch processing margin.

Modification often takes place within a batch process that carefully controls reaction conditions to ensure a consistent product. The economic batch size for many processes is around 1 000 tonnes. This will limit market opportunities as a number of markets will be of insufficient size to warrant production in such low volumes.

Native starches are used to a lesser extent than modified starches in industry due to a number of limitations associated with them. Secondary processing can greatly enhance the suitability of starch for many applications. Some of the limitations of native starches are summarised in Table 6.1.

Table 6.1 Limitations of native starches

insoluble in water at room temperature	subject to retrogradation (see Appendix 1)
lack of specific functional properties	tendency to form rigid opaque gels
variable peak viscosity	break down during extended cooking
excess viscosity after cooking	lack of clarity
sensitive to shear or low pH's	cohesive or rubbery texture of cooked starch
low dispersability of the starch granules	water repellency
granules lack free-flowing properties	failure of granules to swell and develop viscosity in cold water

(Colonna *et al*, 1987; Visser and Jacobsen, 1993; Wurzburg, 1986)

To overcome these problems, starch is further processed after extraction by:

(i) physical, chemical or enzymatic modification

(ii) enzymatic or acid hydrolysis to produce a wide range of oligomeric or monomeric products.

The approach to secondary processing of potato starch is different from that of cereal starch. Potato starch processing is focussed on high molecular weight derivatives, whereas up to 80% of the output of cereal starch processors may be used for production of low molecular weight dextrin. Potato starch cannot compete on the dextrose market as it is more expensive than cereal starch, but it has qualities which have traditionally made it the preferred choice of certain starch-using sectors - for example, paper manufacture. These qualities are not required if potato starch is used for dextrin production and therefore potato starch has no advantage. On the other hand, cereal processors consider that many of the starch-using sectors which have traditionally used potato starch could be supplied by maize starch. They believe that developments in secondary processing will soon give preparation of maize starches with equivalent properties to potato starch but at a lower price, for most applications.

Starch processors are interested in developing bio-technological methods of modifying starches in order to reduce the use of chemicals and the amount of processing. Some of the chemicals used in current processing are hazardous e.g. ethylene oxide and propylene oxide. Other reactions involve the use of organo-chloro compounds. Legislation has blacklisted some chemicals so there is already a requirement to reduce the use of some of these chemicals and also to reduce some emissions during processing. This requirement is likely to be accelerated in the future. In the long term, varieties producing starches already tailored for specific markets may reduce the use of these chemicals, but development of post-harvest modification using bio-technological techniques may more easily be achieved in the short term. An example of this is the enzymatic modification of starch using the prokaryote branching enzyme *in vitro* to obtain a more uniformly branched product (Visser and Jacobsen, 1993).

6.2 Production of starch derivatives

Process engineers Barr & Murphy Overseas Ltd divide starch derivatives into five groups according to processing methods:

Group I	Tank products that require cooking before use
Group II	Pre-cooked cold water soluble products
Group III	Highly substituted starch ethers
Group IV	Roasted starches - dextrins and roasted starch ethers
Group V	Sweeteners, glucose, maltose, isoglucose etc.

6.2.1 Group I Tank products

Group I products can be considered the basic group containing a large number of starch derivatives for food, textile, paper and adhesive applications and consequently more emphasis has been placed on describing these products. Group I products are termed tank products because of their method of manufacture. Starch is slurried and stirred in a tank with temperature and pH control. The tanks are either steam-jacketed or have a pumped circulation with a heat exchanger. After reaction the slurry is pumped to a buffer tank and from there added to a multi cyclone washing assembly. After washing the slurry is concentrated by a vacuum filter or centrifuge. The filter cake is flash dried and usually sifted and/or milled.

The following derivatives fall into Group I:

- Oxidised starches
- Oxidised acetylated starches
- Cross-linked starches
- Oxidised starch ethers
  - (i) starch ethers
  - (ii) (Oxidised) carboxymethyl ethers
  - (iii) (Oxidised) hydroxyalkyl ethers

6.2.1.1 Oxidised starches. The starch slurry is treated with a combination of sodium hypochlorite, caustic soda and sodium carbonate to produce a range of oxidised starches. The oxidation is a combination of hydrolysis of a few inter-glucose bonds and the introduction of aldehyde, carbonyl and carboxyl groups into the starch molecules.

Hydrolysis causes reduction in the average molecular size of the starch molecules (oxidised starches are sometimes classified as degradation products (Anon, 1986)) which promotes the solubility of the starch during cooking and reduces viscosity, thereby allowing starch to be used in higher concentrations.

The introduction of carboxyl- and carbonyl- groups stabilises the viscosity, and so reduces the tendency of the starch to gel. Aldehyde groups are less desirable as they cause viscosity instability and consequently lead to gel formation. However, reaction conditions can be chosen such that the formation of aldehyde groups is minimised.

Oxidised starches are used in the food industry for binding and texturing soups and sauces etc, the textile industry for warp sizing of cellulose yarns and textile finishing, (see Section 7.4.2) the paper industry, for the surface sizing of paper (see Section 7.1.3) and paper coating (see Section 7.1.4), and in adhesives for laminating (see Section 7.6.3). Oxidised starches have specific advantages with respect to transparency and power of penetration (Anon,1986). In general, the granules of oxidised starches resemble those of the native starches from which they are made (Wurzburg, 1986). Production of 1 000 kg of oxidised starch requires 1 040 - 1 050 kg of maize or wheat starch or 1 025 - 1 030 kg of potato starch.

6.2.1.2 Oxidised, acetylated starches. The viscosity stability of the oxidised starches can be further improved by esterifying or etherifying the oxidised starch. The latter process is more complicated but the resulting products cannot be saponified in alkaline conditions. Acetylation of starch is the most frequently used esterification process carried out to give a degree of substitution between 0.03 and 0.1. Acetylation is carried out using either vinyl acetate or acetic anhydride. In addition to improvements in the viscosity stability, other properties like binding power, film flexibility and elasticity are also improved. There are normally about 6 grades of starch esters.

Oxidised starch acetates are used within the food industry, for the production of confectionery, the textile industry for warp sizing of cellulose yarns (see Section 7.4.2), and the paper industry for the surface sizing of paper (see Section 7.1.3).

6.2.1.3 Cross-linked starches. Native starch can be cross-linked by treatment with phosphorus oxychloride. This results in an etherified product, which does not dissolve in hot water, but is capable of swelling to a large extent. Cross-linking essentially substitutes the hydrogen bonds which are responsible for native starch granule integrity with chemically bonded bridges. When a native starch is heated in hot water, the hydrogen bonds will weaken, and viscosity rises to a peak reflecting maximum hydration of the swollen granule. With continued heating, the hydrogen bonds holding the granule together rupture, the swollen granules collapse and disintegrate and viscosity drops. With cross-linked starches the granule may swell as the hydrogen bonds are weakened. After they rupture, however, the chemically bonded cross-links which have been introduced may provide sufficient granule integrity to keep the swollen granules intact and minimise or prevent loss in viscosity (Wurzburg, 1986).

Cross-linking provides:
- high viscosity thickeners
- short salve-like paste textures
- resistance to viscosity breakdown and loss of texture in acidic media
- resistance to mechanical shear
- resistance to viscosity breakdown at high temperatures.

Cross-linked starches are important in the food industry where they are used as thickening agents in soups and sauces and impart better "mouth feel" to products (Anon, 1986).

If the level of the cross-linking is moderately high, there may be sufficient cross-links in the product to interfere with the swelling of the granule so that the viscosity is reduced. At high levels of cross-linking (1 cross-link in 100 or less anhydroglucose units), the cross-link will almost completely prevent the granule from swelling in boiling water. This may have applications in, for example, the production of surgical dusting powders which are required to withstand sterilisation by autoclaving (Wurzburg, 1986). Cross-linking is often combined with other modifications to provide the functionality required by industry.

6.2.1.4 (Oxidised) starch ethers.

(i) Cationic starch ethers. The reaction of native starch with a cationic agent results in the production of cationic starch. Cationic starches are produced with varying degrees of substitution. The positive charge of the starch causes an increase in the retention of fillers and fine fibres in a paper sheet during paper making (see Section 7.1.2) In addition the retention of the cationic starch itself within the paper is complete.

(ii) (Oxidised) carboxymethyl starch. The reaction of native starch with monochloroacetic acid results in an anionic starch ether. This type of product can be used as a warp sizing product for cellulose yarns as well as blends of natural and synthetic yarns (see Section 7.4.2).

(iii) (Oxidised) hydroxyalkyl starch. Reaction of native starch with propylene oxide or ethylene oxide is used to produce a range of non-ionic starch ethers. The use of ethylene oxide requires special gas-tight equipment during the manufacturing process. Hydroxyalkylethers are used in the textile industry for warp sizing of blends of cotton and synthetic yarns due to their good removability (see Section 7.4.2), the paper industry for surface sizing (especially on one sided paper where they minimise curling and when varnish hold-out is desired) (see Section 7.1.3) and the adhesive industry for the manufacture of gummed tape (see Section 7.6.3.2).

The advantage of these ethers over the esters is that no saponification can occur under alkaline circumstances. The ethers show a high binding power, high film flexibility and elasticity.

6.2.2 Group II Cold water soluble products

Group II consists of a number of simple pre-cooked starch products, manufactured by the extrusion of native starches in the presence of chemicals. The resulting products are cold water soluble and can be used in the food industry, the adhesives industry for manufacture of wall-paper adhesives and bill-posting paste (see Section 7.6.3.5), the oil industry for the manufacture of conventional drilling starches (see Section 7.6.3) and for animal feed as calf milk starch.

6.2.3 Group III Highly substituted starch ethers

Group III consists of a number of more sophisticated chemically treated products such as highly substituted, cold water soluble starch ethers. These products can be used in the textile industry as printing thickeners (see Section 7.4.2), the adhesives industry for production of multi-wall sacks, board laminating, aluminium foil laminating, wallpaper adhesives and bill-posting adhesive, (see Section 7.6.3) the oil industry for the manufacture of advanced drilling products, (see Section 7.6) and for cationic starch production for use in the paper industry (see Section 7.1.2).

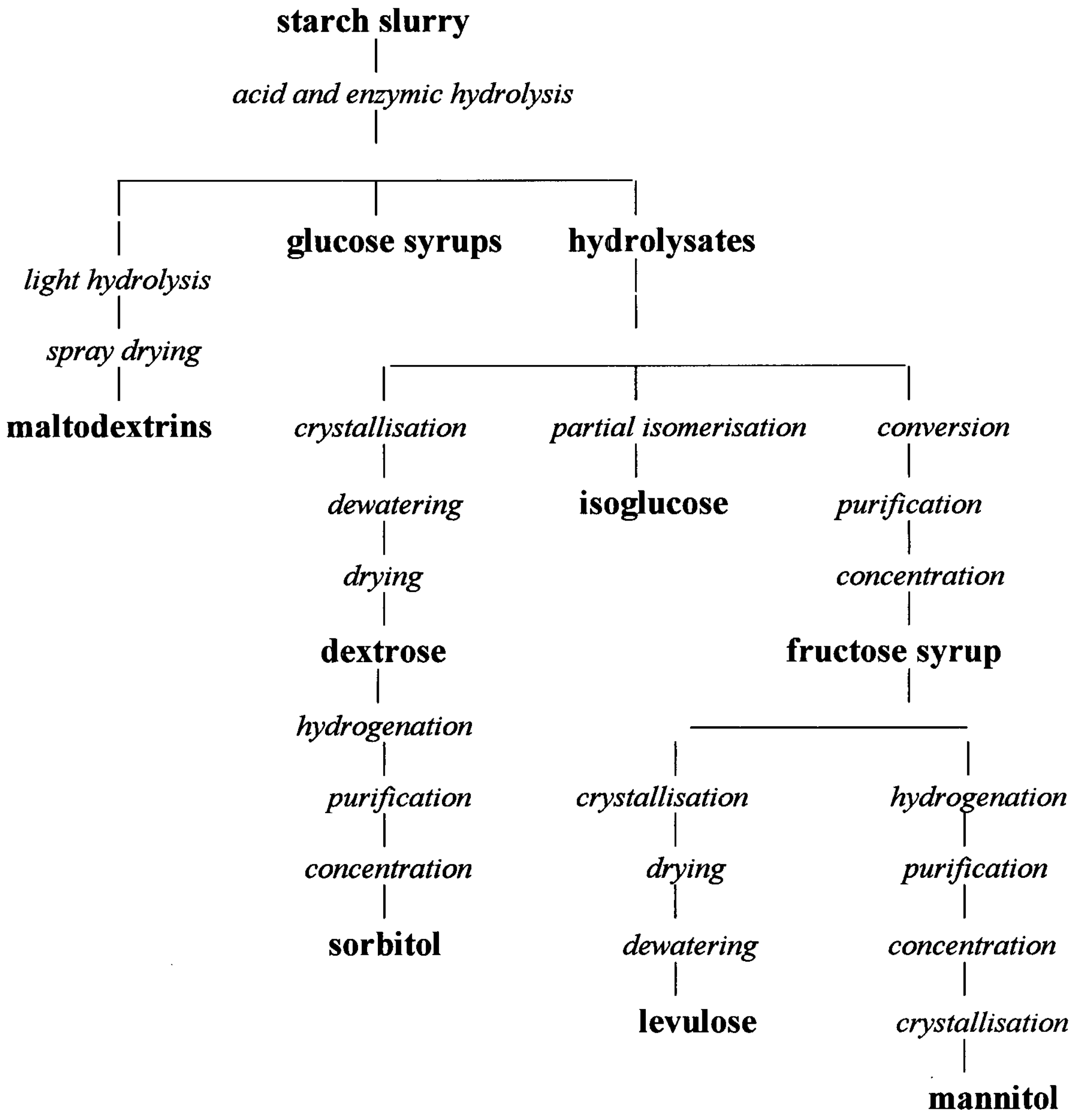
6.2.4 Group IV Dextrins and roasted starch ethers

Group IV products are roasted starches or dextrins, and roasted starch esters, such as starch phosphates and sulphates. Group IV products are produced by mixing the starch with chemicals. Dextrins have been catagorised as "degradation products because they are formed by hydrolysis of starch (e.g. by acid or by dry heat treatment). The resulting products have improved viscosity properties and can be used in the paper industry for surface sizing, paper coating and internal sizing, the textile industry for warp sizing and textile printing, the adhesives industry for gummed tape and adhesive manufacture (dextrins), and the oil-well drilling industry for the manufacture of advanced starch products.

6.2.5 Group V - Sweeteners

"Sweeteners" such as glucose are manufactured for the food industry but these sugars, which can also be categorised as hydrolysis products, also form the basis of a number of non-food products. For example starch is broken down into sugar units for the production of surfactants, and chemical products such as sorbitol and ethanol (see Section 7.10 for examples of markets). The process of hydrolysation involves modification of the starch with acids or enzymes. Hydrolysation can be undertaken to varying degrees. Complete hydrolysation gives 95-98% glucose. Figure 6.1 illustrates some of the various processes and products. Hydrolysis may be carried out by the starch processor, or a manufacturer of for example, sorbitol, may purchase native starch and carry-out the whole production process.

Fig 6.1 Diagram for the manufacture of hydrolysates, including glucose (Anon 1986)



CHAPTER 7 INDUSTRIAL MARKETS FOR STARCH

This chapter looks at a number of industrial sectors in detail, in order to identify current patterns of starch use and assesses potential for the future from the point of view of starch processors and UK agriculture. The sectors which have been chosen include established starch-using industries, some relatively new uses, and sectors which have been identified by the starch processing industry as offering good potential for the future

7.1 Paper and board industry

7.1.1 Background

The paper and board industry is the biggest non-food starch using sector. EU figures indicate that 59% of UK industrial starch use is by this sector (see Table 1.1). The formation of paper is a continuous filtration process in which cellulosic fibres are formed into a network which is then pressed and dried. The process consists of the following steps:

1. Production of pulp - addition of fillers and chemical agents.
2. Forming - applying the pulp slurry to a screen.
3. Draining - allowing water to drain by means of a force such as gravity or a pressure difference developed by a water column.
4. Pressing - further dewatering by squeezing water from the sheet.
5. Drying - air drying or drying of the sheet over a hot surface.

Starch is used in paper making to aid retention of fillers (fillers, e.g. china clay are used to reduce the cost of paper production as they are cheaper than cellulose) and fine fibres on the paper sheet, to improve strength and as a component of coating formulations. In the manufacture of board, starch is used as an adhesive or ply binder and in the manufacture of paper from recycled fibres, starch is added to restore the natural binding qualities to the fibres. Starch use in paper production can be divided into surface sizing, wet end addition and coating.

7.1.2 Wet end addition

The wet end is the initial part of the paper making process where cellulose fibres are mixed with a large volume of water. Starch use at the wet end falls into 2 separate categories, starch added to improve dry strength, and starch added as part of retention systems, although starch added primarily as a dry strength additive will also to some extent function as a retention aid. Consumption of cationic starch (see Section 6.2.1.4(i)) for use as a dry strength agent and as an integral part of various 2 component retention aid systems has increased greatly over the past few years (Georgeson, 1991).

Dry strength additives. Starch is mixed in with the pulp at the wet end to increase dry strength by reinforcing the fibre-to-fibre bonds. Addition of uncooked native starches to the pulp slurry is inefficient due to the unpredictable level of pasting and poor distribution; the starch acts as a filler and decreases strength. Cationic starches perform better. They are retained more fully and consistently, resulting in less transfer to the effluent and subsequently reduced oxygen demand. They are also effective at low dosage levels and are adsorbed and retained on a variety of fillers.

Retention aids. The retention of additives, fillers and fines is important from the standpoint of economics and controlling pollution. Cationic, neutral and anionic polymers are used either singly or in combination as retention aids. The polyacrylamides and polyethyleneimines are commonly used, but colloidal silica is becoming increasingly important and cationic starch is an important component of colloidal silica dispersions.

7.1.3 Surface sizing

The sizing section is the area where the wet-formed sheet may be smoothed and finished by the addition of surface coatings. This segment accounts for most of the starch used in the paper industry. Surface sizing has a number of functions. The process improves the surface strength and printing properties of the paper. Other effects include improved fold, tensile strength, internal bond and erasability.

The use of modified rather than unmodified starch for surface applications has been recommended for a number of reasons (Maher and Cremer, 1986).

(i) A wide range of viscosities are available. Different types of paper require different levels of penetration of the paper by the starch. Viscosity of the starch can be used to control this.

(ii) When paper is recycled, non-cationic starches are not retained on the fibres whereas cationic starches are. Use of cationic starches for sizing therefore reduces the oxygen demand of effluent from mills recycling paper.

(iii) Most modified starches, while thickening on cooling, do not set back or gel. Retrograded starch is less efficient than a non-retrograded starch in improving the strength properties of the paper.

(iv) Hydroxyethyl, hydroxypropyl and acetylated starches have improved film-forming properties.

A range of modified starches are suitable for surface application. These include acid thinned starches[1], oxidised (often termed chlorinated) starches (see Section 6.2.1.1), starch ethers (see Section 6.2.1.2), starch esters (see Section 6.2.1.2), cationic starches (see 6.2.1.4(i)), anionic starches (see 6.2.1.4(ii)), octenyl succinated starches and mill converted starches (i.e. native starch purchased and modified by the paper manufacturer, (see Section 7.1.5) (Erceg, 1984; Maher and Cremer, 1986). A major starch processor considers that there is a growing

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[1] Starch hydrolysed to produce shorter chains than are found in the native starch by treatment in aqueous slurry with acid. This lowers the viscosity.

market for chloride oxidised starches (see Section 6.2.1.1). These can not be made from wheat because of problems with the waste water.

7.1.4 Coating

Coating is carried out to improve brightness, gloss, smoothness,. caliper, colour and uniformity of the base paper by the application of coating mixtures or coating colours - these materials are composed of pigments, additives and binders. Starch is used in coating formulations as a binder and as a thickener. Binders bind pigment particles together, bind the coating to the paper, reinforce the base sheet and fill the pores of the pigment structure. Thickeners control the viscosity and water retention properties. Coating is the smallest of the starch-using sectors within the paper making process. Approximately 20% of papers are coated (Biermann,1993). A specific coating process is carried out at the "calendar stack". The process, originally associated with calendar production is sometimes regarded as a separate stage of paper making. The process is used to give a high quality glossy smooth finish.

Both unmodified and modified starches can be used for coating, however modified starches have improved performance relative to unmodified and are cheaper than synthetic coating products (Maher and Cremer,1986). Starch can be used effectively to extend higher cost latex builders without detracting from the latex properties in the coated sheet and can even improve the performance of a latex.

Modified starches available for use as coating binders include the following:

(i) Starch ethers (see Section 6.2.1.4). These are high quality coating binder starches. They have high adhesive strength, are non-congealing and impart desirable rheological properties. They are available in a wide range of viscosities.

(ii) Starch acetates (see Sections 6.2.1.2). These have good adhesive qualities, are non-congealing and impart the desired rheological properties.

(iii) Cationic starches (see Section 6.2.1.4(i), 6.2.3). These have good adhesive strength and can be made water resistant more easily than the non-cationic starches. However they are more difficult to formulate into a coating colour because they flocculate the pigment.

(iv) Anionic-cationic starches (see Section 6.2.3). These are similar in performance to cationic starches but do not cause pigment flocculation.

(v) Oxidised starches (see Section 6.2.1.1). These perform well as coater-binding starches but cause filler dispersion problems when coated paper is recycled or put through a mill's broke system.

7.1.5 Existing market

The paper and board industry accounted for 127 845 t of starch in the UK in 1993/94 and 929 228 t within the EU. World-wide the consumption of starch in the paper industry has been estimated as 3.6 million tonnes.

A survey of UK paper manufacturers was carried out by SAC for this report in order to gain up-to-date information on starch types used in the industry, and to determine whether manufacturers felt that their needs were being met by the starch industry.

Questionnaires were sent to 104 companies listed in the Philips International Paper Directory. There were 47 returns, 16 from non-starch users. Of the non-starch users, one was from a closed mill, and 4 did not specify products manufactured. Others specified products manufactured but stated that they did not use starch. The products where no starch was used included:

> newsprint; cigarette tissue; tissue; filtration paper; shoe boards;
> handmade artists water-colour paper, bookbinding, millboard and fibre board;
> chipboard; wadding and speciality pulps.

This is in agreement with a report published in 1986 (Anon, 1986) which stated that many paper and board products use no starch or starch derivatives in their manufacture and that most of the starch used in the paper and board sector is used in the production of printing and writing papers and corrugated case materials. The same author noted that while starch is regularly used in some of the other sections of the paper industry listed above i.e. newsprint, tissues and special purpose papers or boards, it is used in very small quantities.

Of the 31 replies from the companies that did use starch, 3 did not specify the quantity used. The remaining 28 accounted for a total of 73 221 tonnes of starch/year. This is equivalent to 57% of the UK's 1993/94 paper and board sector use. Although this is a good level of response, it can give only an indication of the UK situation. A higher return of questionnaires may have revealed a slightly different pattern of use. Certain aspects of starch use are not detailed in this report as they were given in strict confidence. The division of total starch use accounted for in the survey between segments of paper and board manufacture is shown in Table 7.1.

Table 7.1.1 Division of total starch use between different segments of paper and board manufacture recorded by the SAC survey

segment	starch use (% of total)
size	51.2
wet end	30.4
coating	1.1
ply bonding (for boards)	1.0
unspecified	16.3

The split of total starch use accounted for by the SAC survey between maize, wheat and potato starch is shown in Table 7.1.2.

Table 7.1.2 Division of total starch use accounted for by the SAC survey by botanical origin

botanical source	quantity used (t)	%
maize	26 500	36.70
waxy maize	380	0.51
Wheat	12 750	17.40
potato	17 061	23.30
*maize/potato	11 750	16.00
*wheat/potato	2 000	2.73
*maize/wheat	2 000	2.73
*maize/potato/wheat	780	1.07

*Total starch use indicated on returned questionnaires not divided between the types used.

Several references indicate superior performance of potato starch, relative to other starches for use in the paper industry (Swinkels,1992) but only one returned questionnaire stated that potato starch was preferred for its quality in terms of strength, cleanliness and solution properties. An overall preference for potato starch was not indicated from the results of the survey. Quality was a more important factor where potato starch was used but cost was often cited as the most important factor in choosing maize or wheat starch. One manufacturer stated that development of modification processes had reduced the differences between maize and potato starch and both types were now very similar. Another indicated that they used either maize or potato starch and the split of maize/potato was entirely dependent on the economic situation and the contract arrangements with suppliers, whilst a different company indicated that they found cationic maize starch gave the best print properties.

Opinion seems to be divided within the industry on the suitability of wheat starch for paper manufacture. One manufacturer stated that they currently used potato starch for quality reasons but were considering changing to wheat because of the lower cost. The same manufacturer stated that there was a general industry trend away from potato starch to wheat. However another comment was "wheat whilst used is awful for paper making". This opinion was reiterated by some other companies. One manufacturer indicated that the high protein content of wheat starch was a problem and another stated that being both manufacturers and users of starch they would like to get better separation of starch from protein. They find that different supplies of flour perform differently and suggest that work is required to identify varietal characteristics which allow better separation. This company produce starch in a joint venture with a food company - they use the starch and the food company use the gluten.

A specific use for wheat starch was identified by one manufacturer who stated that native wheat starch was used in the coating of carbonless copy papers (e.g. photocopying paper) because of the granule size. In this case the starch was being used to protect the capsules containing the colour forming material. The size of the starch granule was important to provide the correct degree of protection.

The quantities of native and various modified starch types purchased are shown in Table 7.1.3.

Table 7.1.3 Quantities of native and modified starch use accounted for by the SAC paper questionnaire

modification	botanical source	quantity tonnes/annum	% of total
native starch	all	34 470	45.60
	wheat	12 700	17.30
	maize	13 500	18.40
	wheat/maize	2 000	2.70
	potato	6 270	8.50
cationic	all	22 610	31.70
	maize	4 890	6.70
	potato	5 970	8.10
	maize/potato	11 750	16.00
amphoteric	maize	380	0.53
acetylated	potato	1 600	2.25
esterified	potato	1 406	1.97
oxidised	potato	2 205	3.10
cationic/native*	all	10 500	14.70
atomyl	wheat	50	0.07

* Total starch use indicated on returned questionnaires not divided between types.

The use of different starch product types is summarised in Table 7.1.4. Some returned questionnaires did not specify between e.g. cationic and native starch and therefore the information in the following table could only be derived for returns where quantities were specified for individual starch types used.

Table 7.1.4 Use of different categories of starch products as indicated by the SAC paper questionnaire

starch product	use	%
native starch	size	97.0
	coating	2.0
	ply binder	1.0
cationic starch	wet end	98.0
	sizing	2.0
amphoteric waxy maize	wet end	1.0
	bonding agent	99.0
acetylated potato	sizing	100.0
esterified potato	coating	0.5
	ply bond/size	99.5
oxidised potato	coating	9.0
	size	91.0

The results of the survey indicate a pattern of use where manufacturers purchase cationic starch for use at the wet end but tend to buy native starch for sizing. Paper manufacturers modify the native starch on site, by a thermal, thermochemical or enzymatic process to adjust viscosity. The main advantage of on-site conversion for paper manufacturers is the use of low cost raw materials (Erceg, 1984). Thermochemical conversion has the advantage over thermal conversion that it is more versatile in the range of viscosities that it can produce and was the most commonly employed method of modification identified by the survey. Nine manufacturers stated that they thermochemically converted native starch for sizing, as opposed to 2 using thermal conversion and 2 using enzymatic.

Little information was obtained from the survey on the use of starch for coating. Of the starch that was used for coating, small quantities of oxidised and esterified potato starch were used, as well as native wheat starch. It has been suggested that oat starch may be suitable for coating of graphics papers due to its very small granule size. Four manufactures stated that they used starch in coating formulations, 3 of which used potato starch. An additional manufacturer of coated papers was contacted who stated that potato starch was used for coating their papers. Potato starch has very large granules, and it might be expected that if small granule size was desirable more wheat starch might be used. However, coatings contain a wide range of components with different functions and oat starch may be suitable for different functions than potato starch.

7.1.6 Future developments

In general, activity in the paper industry is closely linked to the economic situation. Paper use declines in a recession and increases in more prosperous times. This naturally has a knock-on effect to the starch industry, for which the paper industry is a very large market. There are some indications that the use of starch in the paper and board industry is increasing. Information obtained from The Paper Federation of Great Britain indicated that starch consumption in 1993 had increased to 131 000 t from 120 000 t in 1990, and identified the growing emphasis on packaging from recycled fibres as a factor likely to result in increased starch use in the paper industry. In an international context it may be expected that demand for paper products will increase from Eastern Europe with increasing standards of living. This will be reflected in demand for starch products which is initially unlikely to be met by domestic production.

Some routes to increasing starch use in the paper industry may be to replace some of the synthetic polymers currently used (listed in Section 7.1.7), to allow more cost effect use of fillers (e.g. china clay) and to incorporate higher levels of starch in paper, as a filler. Incorporation of conventional fillers such as china clay reduce the strength of the paper. If addition of starch can effectively compensate for this loss in strength, its use would rise as it would allow manufacturers to increase the levels of filler they incorporate. Sheets of paper have been produced containing more than 60% filler using cationic starch with virtually the same tensile strength as the unfilled sheet without starch (Lindstrom, 1984). Use of starch itself as a filler may have a greater impact on starch use. Work has been carried out which suggests that it may be possible to manufacture for example, cartons with a 50/50 mixture of starch and cellulose (Anon, 1990).

Overall, manufacturers who completed the questionnaire stated that they felt that the starch industry was fully meeting the requirements of the paper industry. However, the following points and suggestions for future developments were made.

- Lower cost, highly modified starches to enhance performance are becoming more necessary. Improved retention of starch in the paper making process is becoming more important. Modifications to the starch or additives to improve retention are very desirable, but not at excessive cost. Cationic starches are known to perform better but are not always cost effective.
- Contamination in deliveries was noted as an issue by one manufacturer.
- Temporary wet strength grades of starch would be useful, for tissue manufacture.
- Modification to improve retention in the sheet and on the paper machine e.g. the production of highly cationised starch would be beneficial.
- There is a requirement for starch products modified to maintain strength (stiffness) properties under moist conditions, also to maintain stiffness without the tendency to crack when board is creased, and possibly polymers to assist in coagulation/flocculation in industrial effluents, as currently used polymers and metal salts are expensive.

- Further modifications to starches to enhance opacity, strength and print performance are always necessary.
- Products to enhance ink jet/laser printability are becoming more necessary.

7.1.7 Inhibitory factors and competing products

Although information from The Paper Federation of Great Britain indicates that starch use in the paper industry is expected to increase, particularly with the growing emphasis on packaging from recycled fibres, it is considered that growth may be inhibited by EU legislative manipulation of the refund scheme. This currently compensates EU industrial users of starch for not being able to get starch at the much lower free world market prices.

Coating formulations. Coating mixtures comprise many different additives. Starches compete with more expensive latex and some cheaper synthetics such as acrylics and polyvinyl acetate as additives, as well as some other natural products (e.g. soya protein), although their different properties complement each other (Anon, 1986). Starch is likely to face increasing competition in the future for this use.

Retention aids. Starch which is added at the wet end to improve dry strength also acts, to some extent, as a retention aid. This has been viewed by the paper industry as a welcome side-effect of its main function. The substances most commonly used specifically as retention aids are synthetic water soluble organic polymers such as polyacrylamides, polyamines, polyethyleneimine and polyethylene oxides. The effectiveness of these synthetic products is related to molecular weight and charge density - if the charge density is low, a higher molecular weight is required to achieve the same functionality. Recent changes in papermaking such as greater use of fillers and recycled fibre, faster machine speeds and a shift to neutral pH at the wet end has resulted in developments of new 'dual component' retention systems. Some of these are dual synthetic polymer systems, but others incorporate starch. One such system is a colloidal silica/cationic starch system which combines the use of cationic wet end starch with anionic silica. Another is an aluminium hydroxide (termed alum within the paper industry)/ cationic starch system (Gill, 1991). Development of these systems may provide an opportunity to increase starch use in the paper industry.

Dry strength additives. Polyacrylamide competes directly with starch as a dry strength additive. However, starch, because of its competitive price is overwhelmingly the most important dry-strength additive used in paper making. About 20 times more starch than polyacrylamide is used for dry strength (Roberts, 1991).

Surface size. Starch is most commonly used for surface sizing, but competing products include carboxymethyl cellulose, polyvinyl alcohol, methyl cellulose, alginates, or wax emulsions.

7.1.8 Conclusions

The paper industry is currently the biggest non-food market for starch and it seems likely that starch use by this sector will increase. Although potato starch has been traditionally favoured for paper manufacture, industry opinion is that starch quality differences are narrowing and that the lower cost of maize is giving it a competitive advantage. This situation has been compounded by high potato starch prices in 1995 which are due to the poor harvest of 1994. The use of wheat starch is also increasing due to its lower cost, although its quality causes concern. The poor harvest of 1994 may result in long term damage to the potato starch industry and the dry 1995 growing season and expected low potato yields may cause further damage. It has resulted in paper manufacturers looking for more secure sources of starch. If they are happy with the performance of maize and wheat products, they may not switch back to potato starch. Therefore, investment in UK potato starch production on the basis of the paper industry is not currently advisable.

The main opportunity for UK agriculture, relating to the paper industry, may lie in exploitation of the emerging trend away from the use of potato starch by encouraging increased use of wheat starch in paper manufacturing. Improvement in protein separation may facilitate this. Most wheat starch currently used by this sector is bought as native starch and modified on site by the paper manufacturer. From the starch processors point of view, this pattern of starch use limits the opportunity for "adding value" to home-grown wheat starch used by this industry.

On a smaller scale, there may be some potential for growing specific crops e.g. oats or quinoa for paper coating where specific granule sizes are required. This is likely to be a relatively small, speciality market which would have much less impact on the UK starch industry than a general shift to use of wheat starch, but may be of interest to starch processors if the starch is of high value to the paper industry.

7.2 Starch-based components for detergent manufacture

7.2.1 Starch utilisation

Detergents are complex mixtures which contain, on average, about 15 different compounds. Interest in starch-derived products in the detergents industry has arisen from an increasing consumer concern over environmental issues resulting in a trend towards more "natural" products. The principal uses for starch in this industry are in the production of surfactants, builders, or sequestering agents and bleaching boosters or whiteners (Leygue, 1993; Röper, 1991).

7.2.1.1 Surfactants. Surfactants are the primary cleaning agents within detergents. They can also act as softeners and anti-static agents, and account for 15 - 20% by weight of detergent formulations. They are low molecular weight amphiphilic molecules consisting of a hydrophilic (water compatible) head group and a hydrophobic (water repellent) hydrocarbon tail. This structure results in the molecule orientating itself so that its hydrophobic group is in a hydrophobic environment. In water, the surfactant molecules will concentrate at the surfaces with the hydrophilic part in the water and the hydrophobic part outside. In cleaning functions, the hydrophobic part of the molecules is attracted to grease or oil. Surfactants are normally anionic or non-ionic but can also be cationic or amphoteric. Anionic surfactants have the biggest share of the market (68% of the US market in 1990) followed by non-ionics, cationics and amphoteric surfactants (USDA, 1993).

Surfactants have a number of industrial uses in addition to their use in detergents. Of the 3.4 million tonnes of surfactants consumed in the US in 1990, 42% were used for industrial purposes, followed by 16% for laundry products and 10% for soaps. Dishwashing accounted for 7%; shampoo 6%; cleaning agents 6%, food processing 5%; cosmetics and toiletries 1% and unspecified other uses 7% (USDA, 1993).

The trend towards natural products in the surfactants industry has two aspects: the use of oleochemical feedstocks for the hydrophobic group and the use of plant-derived carbohydrates to provide the hydrophilic end. In 1990, petrochemical-based surfactants accounted for 52% of US production while oleo-based surfactants had 21% and mixed surfactants 27% (USDA, 1993). Oleochemicals have been used to produce surfactants like lauryl sulphates or alcohol ethoxylates combining a natural oil-soluble group with a synthetic water-soluble group such as ethoxylate or sulphonate. In the development of starch-based surfactants most attention has been focussed on alkylpolyglucosides (APGs). APGs are non-ionic surfactants. They are composed of an oleochemical based oil soluble group and a water soluble group based on glucose derived from starch (See Fig. 6.1) thereby producing an entirely "natural" product (USDA, 1993). There are markets for these products in cosmetic and personal care products as well as in laundry detergents, dishwashing liquids and other cleaning products (USDA, 1993). Chain length determines the application of APGs. APGs with a C10 residue are best suited as co-surfactant for shampoos and liquid soaps, thereby reducing the irritation potential of anionic surfactants. Longer alkyl chain APGs (C12 and C14) are detergent surfactants and even longer alkyl chain APGs (C16 - C18) exhibit emulsifier characteristics and have been proposed for cosmetic and personal care products (Beck, 1995) Without question, detergent manufacturers would be interested in these APG products if they were commercially available at competitive prices.

Although APGs have been described as the non-ionic surfactants of the 1990s (Röper, 1993) other starch-based surfactants also have been developed. The surfactants alkyl glucoside esters, can be produced by esterification of short chain alkyl glucosides with fatty acids (Beck, 1995). In contrast to APGs with the same hydrophobic chain length, these molecules are hardly soluble in water, but exhibit emulsification properties. Their esterification can be carried out enzymically. This offers two advantages over chemical esterification - firstly, a higher selectivity of the reaction and secondly, a process which avoids the use of solvents.

Two other classes of surfactants are the sorbitan esters, a traditional class of surfactants, and products based on N-methyl glucamine, which serves as the starting point for a wide range of surface active derivatives which include cationic, non-ionic and amphoteric surfactants.

7.2.1.2 Builders and co-builders or sequestering agents. Builders and co-builders are multi-purpose additives which buffer the wash medium at alkaline pH, soften the water (by binding hard water ions), promote cleaning and disperse soil particles that are removed during the wash process. They account for 20 - 30% by weight of detergent formulations. They are anionic, have a wide range of molecular weights from low to several thousand Daltons, and include polyphosphates, polycarboxylic acid salts, zeolites, sodium carbonate and citric acid (Paik and Swift, 1995). Tricarboxysucrose (a modified starch derivative) has been proposed by Hoechst as a sequesterant for detergents (Paik and Swift, 1995). Polycarboxylic acids and citric acid can be manufactured using starch as a feed stock (Anon, 1987).

Many investigations are underway to find alternative high performance co-builders from starch-derived products (Koch and Röper,1988). These co-builders should show good calcium and magnesium sequestering properties, synergistic laundry activity, biodegradability and non-corrosiveness. Examples of starch-derived products which have been considered are carboxymethylated products, which act only as anti-redeposition agents, and derivatives from dialdehyde starches which show satisfactory sequestering power, but lack a suitable economic manufacturing process.

7.2.1.3 Bleaching boosters. The necessary technical properties of a bleaching booster can be summarised as

- shifts bleaching activity towards lower temperatures
- compatible with other detergent ingredients
- stable under shelf-life storage conditions
- non-aggressive to fibres
- water soluble
- non-harmful

Bleaching boosters are peracetylated compounds which activate the perborate to decompose at lower temperatures. Starch processors have developed a method for the production of sorbitol- and maltitol-based peracetates, which have been successfully tested at temperatures as low as 40°C (see Figure 6.1).

7.2.2 Starch type used

Surfactants derived from starch are not dependent on the structure or qualities of any specific source of starch. This is because the first step of production involves splitting the starch into sugar units (see Figure 6.1) which are then modified, so cost is likely to be the most important factor in determining the starch type used.

7.2.3 Markets

The detergent sector is a relatively new and developing market for starch-derived products. The European market for the main components of detergent which have potential for starch-derived products has been estimated at 1.3 million tonnes. Leygue (1993) considers that it is possible to replace up to 75% of liquid detergent constituents and 60% of those in powdered detergents, and estimates that an 800 000 tonne EU market could open up to starches in the detergents industry by the end of the decade, but this seems to be an optimistic forecast.

Table 7.2.1 Market size of selected detergent raw materials in western Europe

sequesterates	900 000 t
surfactants	350 000 t
whiteners	50 000 t
Total	1 300 000t

source: Leygue (1993)

Surfactants. Although the starch-derived surfactants APGs have been on the market for 15 years, the quantities used at the moment are small. In 1992 it was estimated that the consumption of APGs was less than 10 000 tonnes worldwide (Branq, 1992). Manufacturers of APGs in Europe include Seppic in France and BASF and Henkel in Germany. In the US, APGs are manufactured by Union Carbide and Henkel and in Japan by KAO.

Recent investments by Henkel have established APG plants of approximately 25 000 t capacities in the USA and Germany. Optimistic market studies have forecasted 100 000 tonnes yearly demand for APGs as a replacement for polyethoxylated alkyl phenols, alkylarylsulphonates and EFA, but these forecasts are unrealistic considering the cost, and conservatism of formulators (Branq, 1992).

Builders and co-builders. Builders and co-builders have been described as the most commercially attractive component of detergents because of the large volumes required and the absence of alternative solutions to replace the non-biodegradable polycarboxylic acids currently used (Paik and Swift, 1995).

European legislation requires the use of 90% biodegradable surfactants. While this legislation may be seen as an encouraging factor for starch-based products, it is important to note that some synthetic products are also biodegradable to varying extents. In addition, the legislation specifies that biodegradable products must be used unless there is no technical solution. This leaves the ruling open to interpretation and subsequently it is not strictly applied.

7.2.4 Potential developments

Surfactants. A great deal of R&D effort is being focused on the development of APGs. Although some APGs have been on the market since 1974, intense research activity only started in the 1980s (Branq, 1992). There is considerable current research activity on alkyl and alkenylpolyglucosides obtained by the acid catalysed alkylation of sugars for use as biodegradable surfactants, led principally by scientists at Henkel and Huls (Paik and Swift, 1995). The level of interest is illustrated by the number of patent applications submitted. During the 10 years prior to 1993, more than 150 patent applications were issued by the leading detergent producers. For example Proctor and Gamble, Henkel, KAO, Unilever, Huls, Rohm & Haas and BASF all applied for patents on either the composition and applications, or the chemistry and process of APG production (Branq, 1992).

Glucamides are another class of carbohydrate-based surfactants which have been developed in parallel to APGs. One representative from this class (lauryl-N-methylglucamide) is currently produced on an industrial scale and is used in dishwashing liquids. Their application is more restricted than for APGs. While their environmental acceptability is generally considered to be good, there are some doubts about toxicological safety as the carbohydrate component (N-methylglucamine) can form a nitrosamine which shows carcinogenic potential in rats.

Overall, the market in carbohydrate surfactants is being carried forward by the requirement for mild, environmentally acceptable products made from renewable raw materials. This is considered to be the most dynamic segment of surfactant development (Ruback,1994).

Builders. Although a successful route to the development of biodegradable polycarboxylic acid from polysaccharides for use as detergent builders has not yet been achieved, work will continue due to the potential size of the market for the products (Paik and Swift, 1995). The main problem has been in obtaining a product that is both functional and biodegradable. A number of companies have been active in this area, including BASF, Rhône Poulenc and Hoechst.

The industry is thought to have accepted the long term need to replace conventional detergent builders (Paik and Swift, 1995). However, conventional builders have no known toxicity problems associated with them and are therefore unlikely to be replaced until a totally biodegradable performance-equivalent is identified which removes any doubts of potential environmental issues. Three approaches described by Paik and Swift (1995) for production of builders and co-builders (oxidation, free radical graft polymerisation and esterification) have not as yet achieved a balance between detergent performance and biodegradability.

7.2.5 Inhibitory factors

Recent developments in the surfactant and detergent industries have been influenced by two distinct factors: the increasing environmental awareness of the consumer and commercial pressures from the market. These pressures have been particularly strong during the recent recession (Ruback, 1994). Since the market for detergents and cleaning agents is the largest segment of the surfactants market, the sensitivity of consumers to price has affected the manufacturing chain from formulators right through to the surfactant manufacturer. There is a demand for more efficient products which achieve the same effect at lower cost.

This financial climate may have had an adverse affect on the development of starch-based surfactants. Although consumers are demanding more environmentally benign products, they appear unwilling to pay a higher price. Starch processors active in this field had very high hopes for starch-based detergent products through the 1980s, but were quickly disappointed.

Companies within the detergents industry have been addressing environmental concerns with respect to their products in a number of ways. These include the production of more compact products and refill packs, as well as the undertaking of new investigations, including life-cycle analysis, in an attempt to provide data to dispel environmental concerns about factors such as biodegradability.

The issue of biodegradability has been addressed in the detergents industry by a switch from using non-biodegradable branched-chain alkyl benzene sulphonate surfactants to their biodegradable linear analogues (linear alkylbenzenesulphonate). This is the leading surfactant in detergent manufacture. It is a petrochemical-based product but is biodegradable, although it will only biodegrade aerobically, which can cause oxygen depletion if discharged into water systems.

The availability of biodegradable petrochemical products in addition to the strong marketing of other environmental developments in detergent products (e.g. reduced packaging) may reduce consumer interest in starch-based products, especially if they are more expensive.

Although starch-based detergents are generally perceived to be more natural and therefore more environmentally friendly than their synthetic counterparts, the chemical transformation of the molecules required to give functionality, depending on the extent, can change or interfere with biodegradability since the enzymes that promote biodegradation of the natural polysaccharide may not work on the modified molecular structure. Therefore testing is always necessary on modified polysaccharides to ensure that biodegradability is not lost. It is difficult to conclude whether starch-based detergents really are more environmentally friendly than petrochemical-based equivalents. Furthermore, starch is not the only polysaccharide with potential for the detergent industry. Carboxymethyl cellulose is currently used as an anti-redeposition agent (Paik and Swift, 1995).

As a renewable raw material APG , however, will have an edge. There is a continual search for renewable raw materials. There is major interest in APGs as new surfactants which can be considered as ecological substitutes to those suspected for their adverse effects on the environment, such as polyethoxylated alkyl phenols (APE) and alkylarylsulphonates (LAS). The ether linkage between glucose monomer and fatty alkyl chains leads to perfectly biodegradable molecules with no toxic residues (Branq, 1992). APG benefits are summarised as follows:

- foam stabilisation
- synergistic effects with anionic surfactants
- no eye/skin irritant effects
- biodegradability under aerobic and anaerobic conditions with no toxic metabolites.

7.2.6 Conclusions

Although the paper or cardboard industry is the largest established starch user, detergents offer the largest potential new market of all the sectors examined. Within the detergents area there is a greater intensity of research into surfactants than builders and bleaching boosters. Interest relates to the biodegradability of starch-based products but modification to improve performance may reduce this property. The selection of starch source is very much price driven as the product is not influenced by the native starch properties. Consequently this opens up opportunities for UK-produced wheat starch, assuming it maintains its current price advantage over maize (see Chapter 5). Many companies are active in product development and much of this R & D work is highly confidential. Consequently Government funded research is more applicable to research of a more fundamental agricultural nature to encourage price competitivity of UK grown crops. A tightening up of the enforcement of European legislation on biodegradable surfactant use would accelerate developments in this area.

7.3 Flocculation products for water purification

7.3.1 Starch utilisation

Water purification involves removal of suspended particles larger than 50 μm by sedimentation. However, many impurities in water and waste water are present as colloidal solids and will not settle out naturally. If these small particles agglomerate, they may reach a size for which removal by sedimentation is possible. Colloidal solids are therefore removed through a process of coagulation and flocculation. Particles are first coagulated by the addition of a primary coagulant such as an aluminium or iron salt. This results in the formation of a microfloc. A polyelectrolyte flocculant or coagulant aid is then used to link the microfloc units together.

Starch-based products have traditionally been used by the water treatment industry as a coagulant or flocculant aid. Starch-based products have, however, been displaced to a large extent by synthetic polyelectrolytes such as the polyacrylamides. These are very long-chain molecules with superior performance, often at lower dosage rates, in high-volume water treatment. Nevertheless, in a number of European countries (for example Holland, France and Belgium) starch-based products continue to be extensively used, as synthetics are discouraged.

7.3.2 Starch type used

Two types of starch-based product are used: non-ionic and cationic cold water soluble potato starches (see Section 6.2.3).

A number of US and Canadian patents indicate potato starch is more favoured over others for use as flocculating agents (Swinkels, 1992). The superior performance of potato starch has been linked to its phosphate content (see Section 3.2.3).

7.3.3 Potential market size

Synthetic polyelectrolytes used in the UK have been estimated at 7 500 tonnes per year. This total includes the following applications:

sewage sludge	2 500 tonnes
drinking water	1 000 tonnes
industrial	4 000 tonnes

The volumes of starch-based products which would be required to replace synthetic polyelectrolytes used in water purification could be up to 10 times higher than the volumes of synthetics currently used, due to the higher dosage rate of the starch-based products. A potential market size of 75,000 tonnes would represent more than 30% of current industrial starch use in the UK. This volume would go a long way to justify a potato starch processing facility.

7.3.4 Competition from synthetic products

The main synthetic products used are polyacrylamides or acrylamide co-polymers. These synthetics are produced with a very wide range of characteristics. The products vary in ionic character, charge density and molecular weight. Companies selling these products advise that tests are carried out to select the most appropriate product from the range. This flexibility and specificity does not seem to be available in the starch-based products currently on the market. Typically only two types of starch-based products are offered.

Starch-based products have a more limited shelf life than polyacrylamides (one year as opposed to two years). Once the products are prepared in solution for use, the starch-based products must be used within 24 hours, whereas the synthetics can retain efficacy over 2 - 3 days.

For flocculant aids, molecular weight is an important factor. The molecular weight of synthetics is much higher than that of starch (20-30 million in contrast to 100 000 - 1 million). The longer the chain, the greater the probability of bridging the small particles, and higher molecular weight polymers often give better sedimentation results

Synthetics are more cost effective than starch-based products. While polyacrylamides are more expensive per tonne, dosage rates are low with many products requiring a dose only 10% of a typical starch product dosage. Starch is used in older water purification plants where there is a slower throughput of water, with a sand filter. Use of synthetics may block these filters because of their larger molecule size. Polyacrylamides are generally used in more modern plants where the throughput is greater.

Biodegradability of the starch-based products may pose a problem rather than be seen as an advantage in this sector. A biodegradable product may increase the biological oxygen demand (BOD) and encourage regrowth of undesirable bacteria.

7.3.5 Conclusions

At first sight the potential for this sector is unclear. Some manufacturers consider this to be a rapidly growing high value market and continue to develop new products, while others have abandoned the market, considering that the starch products cannot compete with more cost-effective synthetics.

However, much of this differing opinion relates to the approach to environmental legislation in individual countries. Enthusiasm for starch-based products is greater in Holland, France and Belgium. It seems unlikely that the potato starch products could be developed to match the technical specification of the vast array of synthetics available. Consequently, any future developments in the UK will be driven by the development of environmental legislation. Clear evidence of the environmental benefits of starch-based flocculants is not apparent. Without this, Government funding for research in this area will be hard to justify.

7.4 Textiles

7.4.1 Existing market size

The textiles industry is a traditional but contracting market for starch. Worldwide demand for starch by the textiles industry has been estimated at 680 000 tonnes (Kraak, 1993), and within the European Community (1990/91) 10 000 tonnes (Leygue; 1993). If the total industrial use of starch within Europe is accepted as approximately 2 773 million tonnes (Röper, 1994), the textile industry only accounts for 0.36% of industrial starch use within the EU. The UK textile market for modified starch is estimated to be around 3 000 tonnes p.a. (1994) or 1.4% of the total UK industrial starch market. It should be noted that the quantities of starch allocated to 'cotton' and 'special textiles' in Tables 1.1 and 1.2 does not reflect total starch usage by the textiles sector. Some of the starch accounted for under 'starch ethers and esters', for example, is likely to contribute to the total textiles use.

7.4.2 Starch utilisation

Starch has 3 principal applications in the manufacture of textiles.

(i) Sizing. Sizing accounts for most of the starch used in the textiles industry. Size applied to the warp forms a film on the surface, and may also penetrate into the fibre bundle. This protects the yarn during weaving by adding stiffness, strength and abrasion resistance. In general, the starch is removed before the cloth is made up into a finished product (Kirby, 1986; Anon, 1986).

(ii) **Printing.** Starch is used in thickeners for dyes and pigments. The use of these products imparts viscosity, improves the quality of printing and leads to efficient use of expensive dyes. The thickeners must be removed after the printing process (Kraak, 1993).

(iii) Finishing. Finishing processes cover blemishes or defects that may be in the yarn, increase bulk, improve the feel of the fabric and add stiffness to products such as the upholstery fabric scrim (Kirby, 1986; Anon, 1986; Kraak, 1993).

In addition to these 3 principal uses of starch, a small amount is used in printing adhesives, used to keep the cloth in place during the printing process. Table 7.4.1 shows the distribution of starch use amongst different segments of the textiles industry.

Table 7.4.1 Starch in textiles worldwide: 0.7 million tonnes

segment	consumption ('000 t)	% of total	starch type used
warp sizing	630	92.6	oxidised starch ethers/esters (see Section 6.2.1)
fabric printing	40	5.9	crosslinked maize (see Section 6.2.1) starch ethers (see Sections6.2.1 and 6.2.3)
printing adhesives	2	0.3	potato starch ethers (see Section 6.2.3)
finishing	8	1.2	dextrins, degraded starches (see Section 6.2.4)

Source: Kraak, 1993

7.4.3 Starch type used

Sizing. The most widely used starch source for size is believed to be potato starch (Anon, 1986). Potato starch has naturally occurring monophosphate ester groups which contribute to its non-gelling, cohesive nature (see Section 3.2.3). It is a good film-former and can be desized with enzyme treatment.

Printing. For screen printing, maize and wheat starch tend to be used rather than potato starch, because they have a smaller granule size (see Section 3.2.1). Potato starch cannot be used at all for state of the art fabric printing.

Finishing. Dextrins and degraded starches are used in finishing products.

Printing adhesives. Potato starch ethers are used as printing adhesives. Some native starch is sold for this purpose (Kraak, 1993).

7.4.4 Qualities required

The qualities of starch products, important for sizing and finishing applications: are viscosity, stability of solution, compatibility with non-starch based sizes, penetration ability, filming ability and gel strength. The starch products applicable to the textile industry can be divided into the following groups (Beersma,1995):

native starches
thin-boiling starch products
dextrins
British gums
starch ethers and starch esters, which are not cold water soluble
cold swelling starches
cold swelling starch ethers

7.4.4.1 Native starches. Starch sizes from unmodified starches are satisfactory for cellulose-based fibres under controlled warp sizing conditions, but they are not the best materials to use for sizing and finishing in all cases. This is due to the high viscosity and poor penetration ability of their solutions. Fabrics which are finished with a native starch have a hard feel and are flat; yarns which have been sized with native starch are brittle and hard (Beersma, 1995). In warp sizing the principal improvement observed when using oxidised and derivatized starches (see Chapter 6) are in smoothness and flexibility.

Derivatization generally improves the desizing of yarns and allows more uniform dyeing after the warp is woven and desized. Native starches are rarely used for sizing, but some native starch is sold for use as a printing adhesive.

7.4.4.2 Thin-boiling starch products. Thin-boiling starch products have lower viscosities than native starches in high solids pastes. They are produced by mild acid treatment which reduces molecular size, but to a lesser extent than in dextrin production (see Section 6.2.4). Fine yarns, which take up size with difficulty, require low viscosity products. Low viscosity products are also recommended for finishing products which require a smooth and full handle, and no colour masking. In addition they are used for very stiff finishes, as required for example in waist bands. Work has shown that hot paste viscosity decreases more rapidly than gel strength. This allows use of higher solids cooks, and more rigid gels per mass unit of starch are obtained. Gel strength is important for abrasion resistance in weaving. Thin-boiling starches can be used in warp sizing of cotton and other cellulosic-based fibres as well as some cotton synthetic blends, but have been superseded by chemically modified products (Kirby, 1986, Beersma, 1995).

7.4.4.3 Dextrins. Dextrins have been hydrolysed to a greater extent than thin-boiling starches and have lower viscosities. "White" dextrins are used for finishing agents, especially if a high loading and a very full handle are required. For example, German manufacturers Emsland-Stärke GmbH produce Emdex, yellow and white dextrins of hydrolysed potato starch, with differing viscosities for the finishing of fabrics.

7.4.4.4 British gums. British gums are degraded starches prepared in the dry state by the action of heat. These products, which are sometimes categorised as dextrins, can be used as printing thickeners

7.4.4.5 Hot-swelling starch ethers and esters (see Section 6.2.1). Etherified and esterified starches do not undergo retrogradation and therefore their solutions are more stable and can be removed more effectively than thin-boiling starches. Ethers and esters with a relatively low degree of substitution are used for sizing and finishing (Beersma, 1995). They are the most commonly used starch-based sizing products.

Hydroxyethyl starch (a starch ether derivative) has a superior filming ability which is useful in sizing cotton synthetic blends (Kirby, 1986). Synthetic fibres do not have the water absorptive capacity of cotton and so a differential arises during sizing of the synthetic fibres and the cotton fibres. Therefore formation of a film on the surface of the fibre is important. Hydroxyethyl starches are suitable for low temperature sizing of worsted yarns, wool mixtures, fibres that shrink on drying and other fibres that cannot tolerate a high temperature. They are compatible with acrylic and other resins used in finishing applications.

Starch acetates are esters which are used for sizing cotton, cotton polyester blends and other synthetic fibre blends. They may be used in low temperature sizing (Kirby, 1986).

Examples of starch ether products on the market include Emsland-Stärke Emsize E, E 4 and E 5. These are esterified potato starch products available in different viscosities. They are hot water soluble and can be used for all spun fibres: cotton, linen, wool, rayon staple and all mixed yarns, and enzymatic desizing is necessary. Emsland-Stärke also produce Emsize E1, E2, E9 and KOH 100 - hydroxypropylated potato starch ethers for use as sizing agents with all natural and synthetic yarns and mixed yarns. Characteristics of these products are the availability of materials with different viscosities, high adhesiveness, and good elasticity in the starch film, which confers high abrasion resistance to the yarn. These products can easily be removed from the fabrics by simple washing treatment.

7.4.4.6 Cold-swelling starches (see Section 6.2.2). Cold-swelling starches are soluble in cold water. They have a reduced tendency to retrograde.

7.4.4.7 Cold-swelling starch ethers (see Section 6.2.3). Cold-swelling starch ethers can be used as printing thickeners (Beersma, 1995). Emsland-Stärke produce "Emprint", a cold water soluble etherified starch which is anionic, for rotary screen printing. It is suitable for use with all dyestuffs except reactive and basic dyestuffs.

Cold-swelling starch ethers are also used as size. Sodium carboxymethyl starch is compatible with the synthetic sizes polyvinyl alcohol (PVA) and carboxymethyl cellulose, and can be used for sizing of polyester cotton blends (Kirby, 1986). Emsland-Stärke produce "Emsize" carboxymethylated potato starch in different viscosities which is cold water soluble and has high adhesiveness for use with polyester/mixed yarns, cotton and rayon staple. The product can be removed from the fabric by simple washing treatment.

7.4.5 Inhibitory factors

Two principal reasons for the decrease in consumption of starch in the EU textile industry are the overall decline in the European textiles industry and the increased use of synthetic sizing products. There has been a shift in the location of woven textiles manufacture to low labour cost countries, for example, in S E Asia, China and India. The industry in these countries, however, still relies heavily on starch-based sizes with the type of starch varying from country to country depending on local availability. It has also been reported that less starch is being used in textile printing as the use of pigment dyestuffs increases. In this system the pigment is glued to the fibre surface using acrylics and no starch is required. Starch derivatives (mainly starch ethers and starch gums) are still important in certain types of vat and reactive printing, but often in combination with other ingredients such as synthetics, alginates, and other natural gums (e.g. guar and locust gum and their derivatives). In addition starch-based stiffeners used in finishing also face competition from synthetic products (Anon, 1986).

7.4.6 Performance relative to petrochemical competitors

Sizing. Synthetic sizing products generally are more expensive than starch-based products. The increase in their use is due to their superior performance. A major advantage of synthetic sizes appears to be in the ease of application and removal. They are water-soluble without the need for cooking, and do not require the use of enzymes for their removal. There may be fewer problems with effluent disposal than for starch-based products although some sources suggest that low biodegradability of synthetic sizes may favour starch products depending on future environmental legislation. The use of synthetic sizes can result in energy savings because they do not require cooking, and can be applied to the warp at lower temperatures.

The development of synthetic fibres and natural/synthetic fibre blends, e.g. polycotton, is considered to have increased the market for synthetic sizes. Starch-based sizes do not adhere well to the synthetic fibres. This may be due to the fact that natural fibres tend to be hydrophilic while synthetic fibres are hydrophobic (Kirby, 1986). The function of the size varies slightly between natural and synthetic fibres. The most important function of sizes for natural fibres is to stick the hairy regions onto the yarn, whereas in synthetic fibres it is necessary to stick individual fibres together.

Finishing. For most sophisticated finishes, such as crease resistance and drip dry finishes, synthetics are used. However, starch and starch derivatives are used as a filler which increases the bulk and alters the finished appearance and feel of textile products. A variety of less viscous starch derivatives are also used. This particularly applies to certain low value products where bulk is important (e.g. cheaper cotton suits) and to certain products where rigidity is required.

7.4.7 Conclusions

Starch is still important in the textiles sector because starchy products are generally cheaper than synthetics, although the poor potato harvest in 1994 has pushed up the price of potato starches for 1994/95 making synthetics relatively more competitive. Starch-based sizing products are often used in blends with synthetic products to achieve a balance between cost and quality.

Research work is being carried out on sizes, particularly in the USA where the cotton industry is important, but this tends to be directed at the development of synthetic sizes. Little or no research of this kind is carried out in the UK. It has been suggested that there is still room for research into modified starches for the textiles industry. However, as the textiles market continues to decline, any products developed would have a very small market in Western Europe.

7.5 Plastics

7.5.1 Starch Utilisation

Research interest in the use of starch for the production of plastics dates back to the 1940s (Griffen, 1994), although there was no commercial development in this area until the 1970s.

The first commercial starch-containing plastic was developed by the UK company Coloroll in the 1970s, in order to produce shopping bags with a paper-like texture (Griffen, 1994), but the degradability of these materials has been the most important factor in their subsequent development. More than 100 million tonnes of municipal solid waste (MSW) is estimated to be produced every year in Western Europe. Plastics account for 5 - 10% of this weight but 25 - 30% of the volume (Koch *et al.*,1993). Volume is a critical factor in landfill disposal as existing sites are rapidly reaching capacity and identification of new sites is becoming increasingly difficult. It has been suggested that the use of degradable plastics could help to alleviate this problem (Röper *et al.*, 1993; Griffen, 1994) as well as reducing the world's dependence on non-renewable resources.

The use of starch for the production of plastics can be divided into three major categories: loaded products, polymer mixtures and thermoplastic starch products.

7.5.1.1 Loaded products. These are manufactured by mixing starch granules directly with the synthetic polymer, allowing starch granules to be dispersed throughout the material. Starch content is generally limited to about 10% or less by weight (Shogren *et al.*,1993). Loaded products were the first starch-containing plastic products developed commercially. The work was sponsored by the UK company Coloroll Ltd. Although this company has collapsed, bags of this type are still manufactured, and continued research and development has resulted in the production of materials that can be processed by a range of methods including injection moulding and bottle blowing.

7.5.1.2 Polymer mixtures. These products are manufactured by mixing synthetic polymers and gelatinised starch together at a molecular level. Reported levels of starch incorporation vary. Shogren *et al.* (1993) state incorporation is up to 50%, while Carruthers and Vaughan (1994) refer to incorporation levels of between 60 and 75%. Novamont produce a starch polymer blend called Mater-Bi containing up to 60% starch. Novamont have produced films as well as rigid products such as pots, bowls and plates containing more than 50% starch (Röper *et al.*, 1993). Similar products are being developed by other companies.

7.5.1.3 Thermoplastic starches. These materials are starch-based rather than starch/synthetic blends. Thermoplastic starches are produced by subjecting native or modified (high amylose) starch to conditions of high pressure, temperature and moisture on a twin screw extruder (Röper *et al.*, 1993). The key characteristic of thermoplastic materials is that they soften on heating and return to their original form on cooling. This characteristic allows them to be processed by injection moulding. The synthetic polymers polyethylene, nylon, polyvinyl chloride (PVC), PTFE, perspex and polystyrene are all thermoplastic polymers.

Thermoplastic starches have been produced containing between 75 and 95% starch and can be extruded like traditional synthetic polymers. However, stability problems at humidities greater than 80% still have to be resolved (Röper *et al.,* 1993). Several institutes and companies are reported to be working on the optimisation of these products. A potato starch-based thermoplastic has been developed by Avebe with ATO-DLO. It has been suggested that the product would be used for a broad range of applications such as packaging materials, foams and trays. The most successful product to date, however, has been stoppers for use in slaughter houses. The stoppers are used to prevent gut leakage.

National Starch manufacture a starch-based protective loose fill material called Eco-Foam. The product, which is a substitute for expanded polystyrene beads, was introduced to the market in 1990 (Anon, 1992) and is reported to have performed well (National Starch Annual Report, 1994). Several other companies are developing foamed materials (Koch *et al.,* 1994). Biopac, for example, uses a modified-waffle making technology to produce foamed starch articles for tray packaging; Sudstarke is producing loose fill materials based on potato starch, and Storopack makes similar products based on maize starch.

7.5.1.4 Other products.

Biopolymers with a polyester structure. These materials are not based on starch but their development may have an impact on the starch industry as starch hydrolysates can be used as a nutrient feedstock for the production of biopolymers through a fermentation process. Two biopolymers have been identified according to Röper *et al.* (1993): poly-ß-hydroxybutyric acid (PHB) and polylactic acid. PHB is made by fermenting bacteria whereas polylactic acid is produced by the chemical polymerisation of lactic acid, resulting from fermentation. PHB has been manufactured by ICI under the name "Biopol" since 1981, and the lactic acid polymer is manufactured by Union Carbide.

Polyethylene and PVC. Starch could be used as a feedstock for the production of polyethylene and polyvinyl chloride following a pathway of starch -> ethanol-> ethylene-> polyethylene (Clements and Antal, 1990).

7.5.2 Market potential

Despite the long-standing industrial and academic interest in the use of starch for the production of plastics, the existing market for starch in plastic manufacture represents a very small proportion of starch use. EU figures indicate that the plastics sector accounts for 40 283 t (1.7% of industrial use starch) in the EU, and 6 777 t in the UK (3% of industrial use starch). These figures include starch used in coating conventional plastic bags to improve print quality, and coating the inside of bags to improve ease of opening. Therefore the quantity of starch actually used in the production of plastic materials is less than the quantities indicated above.

7.5.3 Market developments

Any estimation of the potential market for starch in plastic manufacture is difficult, as opinions on the future of these products are mixed. Some companies continue to develop products and forecast an increasing demand. National Starch, for example, forecast that the 1990s will see greatly expanding markets for Eco-Foam in the US, while other manufacturers, for example, Warner Lambert are reported to have stopped work on long-standing projects. Future demand for degradable plastics will be highly dependent on factors such as consumer attitudes, legislative and regulatory action and the success of recycling and other solid waste programmes (Röper *et al.*, 1993; Pettijohn, 1992).

European waste policy. The European Parliament favours a policy of "prevention" with respect to waste management, and has called on the Commission to research and draw up European taxation policies to encourage waste prevention. Any resulting policies are unlikely to specifically encourage the use of degradable plastics. Rather, the aim will be to encourage recycling, re-use and incineration for heat and power generation, with landfill disposal seen as a last resort. As the main benefit of widespread use of degradable plastics comes from their ability to degrade when disposed of, policies put in place specifically to discourage disposal of waste are unlikely to encourage and may act against the development of markets for these products.

Other polices. Italian legislation originally favoured the use of degradable plastic packaging, but changes to the regulations in 1991 resulted in a greatly depressed market for any new materials. A levy is still placed on plastic packaging, and degradable plastics are no longer exempt. However, Denmark, Switzerland and Sweden have policies that specifically encourage the use of biodegradable plastics (Röper *et al.*, 1993).

Recycling programmes. The success of recycling programmes is dependent on the market demand for recycled products. The European Parliament has noted that the cost of virgin materials does not reflect the environmental cost of their use. A requirement for the use of a minimum percentage of recycled materials in certain products has been suggested by the Commission (European Parliament, 1991) but there is no indication of whether this will be adopted as policy.

Incineration of solid waste. Incineration of waste, irrespective of its biodegradability, reduces the requirement for landfill space and can be used to generate heat and power. Some UK local authorities (e.g. Grampian Regional Council) are actively pursuing this option in order to reduce landfill requirements and to reduce dependence on fossil fuels. Taking into account the emphasis placed on avoiding landfill disposal by the EU, it seems unlikely that a significant market for degradable plastics will be created in the short term through European waste management legislation.

Niche markets. The emphasis on prevention policies in waste management has led to the suggestion that use of degradable plastics would be most valuable in certain niche markets.

(i) Maritime industry. The Marpol treaty which prohibited the dumping of non-degradable articles in the sea after January 1, 1994 should create a demand for degradable products for the maritime industry.

(ii) Items likely to end up as litter. It has been suggested that there may be opportunities for the use of degradable plastics for applications where recycling is impossible or highly impractical. It can be argued that while toys, bottles and other containers are easy to recover and recycle, small plastic wrappers and packaging materials that are common litter problems may be more costly and difficult to recover, and the use of degradable materials may be beneficial in these cases. However, the impact that degradable plastics could have on the litter problem is unclear as, for example, city streets where litter is often a problem, do not provide optimum conditions for biodegradation, and litter is likely to be collected long before it could degrade. Ironically, the use of degradable plastics for production of wrappers might encourage litter dropping and these degradable plastics would retain their integrity long enough to present a problem.

(iii) Bags for composting. It has been suggested that degradable bags could have a market in the collection of material for composting. Leonas (1990) describes an example of the use of biodegradable bags for collection of garden waste in Urbana, Illinois. The bags were used as part of a programme implemented in 1988. The collected garden waste was composted or processed into wood chip or mulch. The use of degradable bags reduced collection cost by 30% because removal of the waste bag was not necessary. However, Cole and Leonas (1990) found that degradation rates of the material were less satisfactory than simulations had predicted, and it was concluded that there was a definite need to accelerate the disintegration of all bag formulations if the turn-around time for composting is less than a year. The authors emphasised the need for testing degradable plastics under realistic rather than ideal conditions. The development of this market for degradable plastics would be dependent on the establishment of programmes to collect material for composting. This would fit in with EU waste management policy but the success of such a scheme would be dependent on the market for the final product.

(iv) Agricultural mulch films. Work has been conducted on developing degradable films suitable for use as agricultural mulch films. The film is placed over the seedbed to warm the ground and thus extend the growing season. It is designed to start degrading as the seed germinates and to have completely degraded by the time the ground needs to be cultivated. Use of degradable film eliminates the cost of removing the film. EU consumption of agricultural mulch films was 370 000 tonnes in 1989 representing a potential 10% of current industrial starch uses.

(v) Medical uses. Degradable plastics may be suitable for certain medical uses such as dissolving sutures, bone pins, drug delivery devices and wound dressings.

(vi) Electronics packaging. A specific starch market could be for the protection of electronics as starch foam is more antistatic than normal plastic foams Frische (1990).

7.5.4 Starch type used

Several publications have identified high amylose content as a desirable quality of starch for use in plastic production (see Section 3.2.2). During the 1950s it became established that the amylose fraction was preferable to amylopectin with respect to use as a solid material (Griffin, 1994). There was some success in producing films from high amylose maize starch at that time but technology was never developed beyond pilot plant demonstrations. More recently, Altieri and Lacourse (1990) at National Starch and Chemical found that high amylose maize starch was most suitable for the production of starch-based protective loose fill material. Chemical modification of the starch by hydroxypropylation improved the qualities further. High amylose starch is also preferred for the production of biodegradable thermoplastics, and Batelle of Frankfurt have used high amylose starch from a number of sources (Frische, 1990). These include amylose separated from common starch, high amylose maize starch and high amylose pea starch, for the development of starch-based plastics. Products have included films, injection-moulded products and extruded foams.

Granule size. For use of starch as a filler, granule size has been identified as an important factor (see Section 3.2.1). The work carried out by Coloroll in the 1970s (see Section 7.5.1) used starch as a filler. It was found that potato starch granules were too large for the required film thickness of 40 - 50 μm. Granules must be small enough to fit into the plastics. Rice starch was more suitable in terms of particle size but was too expensive. The most attractive commercially available starch at the time was maize, although the granule size was not ideal, and had an adverse affect on the tensile properties of the films. However a combination of chemical and physical treatments can be used to prepare small particle granular maize starch (Jane *et al.*,1990).

Modified starches. The highly hydrophilic nature of starch is not compatible with hydrophobic plastics. Use of oxidised polyethylene (OPE), which carries highly hydrophilic carboxyl and carbonyl groups, in starch polyethylene films results in increases in tensile strength and the elongation rate of the film. OPE may act as a bridging material which has its hydrophilic groups interacted with starch while polyethylene chains are blended into the plastic matrix. The carboxyl and carbonyl groups will also enhance the biodegradation of plastic molecules such as polyethylene thus causing problems in the production of polymer mixtures. Chemical and physical modifications of starch to enhance the compatibility between starch and polyethylene have been examined. Films made with octenylsuccinate starch gave better tensile strength and elongation rate, particularly at 15% starch level, than film made with native maize starch. This modified starch also dispersed better in the mixture than the native maize starch.

7.5.5 Inhibitory factors

Factors which are likely to inhibit the development of biodegradable plastics are the low price and high quality of the traditional petrochemical products. In addition, developments in recycling plastics and the effects of the recession, which discourage practices which are beneficial to the environment at a financial cost will tend to slow down developments in this sector. The petrochemical plastics industry has been developing its products for 50 years and it will be some time before starch-based products reach the same level of performance.

Although the plastics industry could potentially be a very large outlet for starch, it is a very difficult market. Five years ago the outlook seemed more optimistic and it was thought that if degradables could secure 5% of the market it would be sufficient to justify production. However, today it appears that even 5% of the market is optimistic.

7.5.6 Economics

Approaches taken to improving the economics of starch-containing plastics to date have been primarily concerned with developments in processing, rather than developments in crop varieties or secondary modification.

Loaded products. US manufacturers Archer Daniels Midland made an important development in the manufacturing technology by bringing wet milling of maize, intense drying of starch and the making of the starch/polymer masterbatch all into the same plant. This vertical integration created a plant with attractive economic benefits, many of which related to energy conservation, obtained as a result of introducing the hot starch into the mixing operation without the need for cooling and storing.

Synthetic/starch blends. The cost of synthetic co-polymers and the processing requirements of the manufacturing stage result in a market price for synthetic starch blends of around three times the price of similar products made from low density polyethylene (LDPE) (Griffin, 1994). Economies of scale will probably reduce prices but they are unlikely to drop below twice the price of LDPE.

7.5.7 Conclusions

Starch- based polymers offer biodegradability and a means to alleviate the problem of the shortage of landfill sites. This degradability is available at higher cost although recent developments in processing have reduced the price differential. Legislation would be required for their widespread use. However, a general policy move by the EU away from landfill disposal and towards recycling and incineration may limit these products to niche markets.

Some success has been seen in this sector particularly with loaded products which were the first commercial development of starch-containing plastics. The production of oat starch with its small granule size may offer an opportunity for UK agriculture, but to a certain extent loaded products are being superseded by polymer mixtures and thermoplastic starches. Granule size is not an important quality for production of these newer materials, so this potential for UK agriculture may be limited. The recently produced starch-based foam packaging materials are making inroads, particularly in packaging high value goods where the companies' improved environmental image is seen as beneficial. The development of starch-based agricultural mulch films merits further work. Quantities of conventional products used in the EU are equivalent to over 10% of current industrial starch usage. Developments in this field would also offer environmental benefits.

7.6 Adhesives

7.6.1 Starch utilisation

Adhesives are a traditional application for crop starch. As starch-based adhesives are normally provided in an aqueous solution, their use is limited to applications where at least one of the substrates to be bonded can absorb water, e.g. wood or paper (Onusseit, 1993), and starch-based adhesives have been used primarily for bonding paper, for example in the manufacture of corrugated board and paper bags.

The utilisation of starch as an adhesive can be divided into six specific market sectors:

(i) Corrugated board. This is the most important sector for starch-based adhesives. Corrugated cardboard is produced on machinery which converts flat paper into corrugations. Adhesive is applied to the tips of the flutes, bonding them to a second sheet of flat paper, or liner board.

The key requirements of a corrugating adhesive are: consistent bond formation; strong initial tack to hold the liner and fluting in position until the permanent bond is formed; stability so that the bond will not deteriorate during storage and handling; and economy in use.

Starch-based adhesives are generally prepared on site by the corrugator, by a variety of methods such as the Stein Hall and the No-Carrier systems.

The Stein Hall system. In this system, 80 - 90% of the starch is applied in the form of ungelatinised starch granules. After the adhesive has been applied it is heated to above the gelatinisation temperature producing a very viscous and tacky paste which will rapidly bond two paper substrates. Ten - 20% of the total starch content of the adhesive is gelatinised prior to application. This high viscosity fraction acts as a "carrier" to prevent the starch granules from settling out and provides the initial tack. The Stein Hall system gives adhesives which are particularly suitable for very absorbent paper.

The No-Carrier system. Unlike the Stein Hall system, this system does not contain a carrier portion. No-Carrier adhesives require more care during preparation than Stein Hall, but perform better. At high production speeds, the short non-elastic texture of No-Carrier adhesives allows precise starch application on the flute tips without splashing into the valleys. Starch manufacturers have developed modifications of this process (e.g. the Minocar system by Cerestar) for which the reaction conditions are less critical than those for the traditional No-Carrier system. With Minocar there is a greater degree of swelling at lower temperatures and the speed of viscosity rise is less dependent on the temperature, allowing finer control of the process.

(ii) Gumming. Starch-based adhesives are used in the production of gummed tape (i.e. tape which is wetted before application). In the gummed tape industry starch has substantially replaced animal glues.

(iii) Paper bags. Starch-based adhesives are used in paper bag manufacture, for sealing bag sides and ends.

(iv) Wallpaper paste. This is the traditional method of attaching wallpaper to walls. For those without a knowledge of the starch industry, this is the most apparent non-food use of starch.

(v) Ready to use adhesives. In the corrugating, bag making and gummed tape markets, starch-based adhesives are prepared by the user. However, starch-based adhesives for use in some other markets such as bottle labelling are prepared by formulators, "ready to use".

(vi) Laminating and tube winding. Starch-based adhesive is used in the manufacture of laminated board (i.e. where two or more plies of paper board are laminated into a solid board), paper-lined foil (e.g. for confectionery wrappers) and cardboard tube winding.

7.6.2 Existing market size

The total world market for starch-based adhesives has been estimated as 1.4 million tonnes. This is split between the starch adhesive using sectors as shown in Table 7.6.1.

Table 7.6.1 Starch use in the adhesives sector

segment	**consumption ('000 t)**
corrugated board	1200
gumming	30
paper bags	40
wallpaper paste	20
formulators	100
laminating/winding	10
total	**1400**

(Source: Kraak, 1993)

Recent estimates of starch use by sector in Europe do not give a specific figure for the total amount of starch used in adhesives. However, the vast majority of starch used in adhesives is used for the production of corrugated cardboard. The corrugated cardboard industry is estimated to have used 8% of total starch production in Europe in 1994. This is equivalent to 480 000 tonnes of starch (Röper, 1995). Table 1.2 indicates that 2 187 t of starch were used in the production of "animal glues" and 3 587 t were used in the production of "glues" in 1993/94. This gives a total of approximately 485 774 t of starch used in adhesives in the EU. There are no figures to suggest that corrugated board production is anything other than dominant in this sector in the UK.

Presumably, as with paper production, the use of starch-based adhesives will rise and fall in line with the economy, i.e. during recession demand will fall and when the economy improves, demand for products such as corrugated board for packaging, are likely to increase. Therefore the western European starch industry is likely to benefit from increasing standards of living in eastern European countries if their domestic capacity cannot supply demand.

7.6.3 Starch type used

Each of the various adhesive applications have their own specific requirements. Specific properties are obtained from various combinations of botanical sources, amylose/amylopectin ratio, modification and use of chemical additives. Overall **maize** starch is most commonly used for **corrugated board** adhesives, but Tables 1.1 and 1.2 show that for production of "**glues**" and "**animal glues**", **potato** starch is most commonly used.

7.6.3.1 Corrugated board. Virtually any starch is usable in corrugating adhesive (Williams, 1986), but maize starch is most commonly used (Kraak, 1993; Cerestar product information, Cerestar UK Ltd, Trafford Park, Manchester). Most of the starch is purchased as native starch, although some may have undergone simple acid or oxidation treatment to reduce molecular weight. A small amount of high amylose starch may be used as the "carrier" portion of corrugating adhesives where their resistance to shearing stress, their higher film strength and inherent reduced sensitivity to water may in some circumstances justify their extra cost. National Starch, for example, offer to this market speciality "genetically hybridised, chemically modified" carrier starches.

The properties of native starches used in corrugated board manufacture are improved and altered by the addition of sodium hydroxide and borax. These chemicals are used in both the Stein Hall and No-Carrier systems to reduce gelatinisation temperature, improve the initial tack of the adhesive and increase shear stability.

7.6.3.2 Gummed tape. It is important that the starch used in gummed tape manufacture has little or no tendency to retrograde in the dry film (Williams, 1986). This property can be achieved by using low amylose starches (see Section 3.2.2) and/or modifications such as esterification or etherification (see Section 6.7.1) of cassava, potato or waxy cereal starches. Potato starch ethers are an example of starch commonly used in the production of gummed tape (Kraak,1993).

7.6.3.3 Formulators. A considerable quantity of different starch derivatives, including dextrins, are used by formulators as components of adhesive compositions, for example, in bottle labelling and envelopes. A popular type of bottle labelling adhesive, jelly gum, is made primarily from the more cohesive starches, such as root (e.g. cassava) or waxy maize starches, which have been cooked in sodium hydroxide (Kraak, 1993; Williams, 1986)

7.6.3.4 Paper bags. The manufacture of paper bags requires the use of two different types of adhesive. "Seam paste" is used to seal the sides of the bag i.e. to form a tube from a sheet of paper, and "bag bottom" paste is used to close the end of the bag. The two types of adhesive have different qualities. Seam pastes are required to develop a strong bond quickly to facilitate a high speed manufacturing process, and contain "white" dextrins (Section 6.2.4). White dextrins are produced by heating powdered starch at relatively low temperatures to promote conversion without excessive colour formation, as opposed to British gums which are converted by heating at relatively high temperatures and are darker in colour (dextrins can be produced from any starch source) are often used for their preparation. However, texture is a more important quality than setting speed for bag bottom pastes. Unconverted starches with a short texture such as maize and wheat are used in the production of bag bottom pastes (Williams,1986; Kraak, 1993).

7.6.3.5 Wallpaper paste. An important characteristic of wallpaper pastes is "slip", or more technically, low shear resistance. An adhesive with good slip properties will allow a piece of wallpaper to be positioned after it has been applied to the wall. Although native potato and cassava starches have low shear resistance, most native starches do not possess adequate slip characteristics to be used as wallpaper adhesives without modification. The type of treatment which imparts a salve-like texture to the starch hydrosol is required. Cross-linked starch ethers (see Section 6.2.1) are normally the starches used in wallpaper adhesive. Some other possible modifications are carboxymethylation, hydroxyalkylation and esterification (Williams, 1986).

7.6.3.6 Laminating and tube winding. Oxidised starch ethers and dextrins are used for this segment of the adhesives industry.

7.6.4 Competitive pressures

Although starch use in adhesives has declined due to strong competition from synthetic products (in 1986, it was reported that starch use for adhesives was only one fifth of the quantity used 10 years previously, due primarily to competition from PVA (Anon, 1986)) starch adhesives are expected to maintain their current position within the adhesives market. There are three reasons for continued use of and need for starch-based adhesives (Onusseit,1993):

1. Starch is one of the few highly polymeric substances with which it is relatively simple to produce aqueous colloidal solutions with a high initial adhesive strength.

2. As a renewable raw material the supply of starch is assured.

3. Starch is a natural product and may therefore be preferred over synthetic adhesives for some markets. For example there is a trend towards replacing synthetic adhesives with starch-based adhesives, particularly in the food processing industry. In addition, the use of starch-based adhesives has been considered in relation to waste avoidance in the packaging materials industry due to their biodegradable character.

The market for starch-based adhesives has, however, been steadily attacked by synthetic products such as polyvinyl alcohol, polyvinyl acetate, acrylate dispersions and hot melts (Kraak, 1993). These synthetic products have increased their market share as high performance adhesives developed for a wide range of specific requirements, such as the need for an extremely rapid tack, more water resistance, or suitability for use with highly finished papers used in packaging, and plastic substrates (Onusseit, 1993; Kraak, 1993). In addition these products may be easier to handle and prepare than starch-based adhesives.

Surface-coating of glass bottles to reduce weight and increase strength has led to increased use of casein-based products at the expense of starch-based adhesives. New developments in starch derivatives in conjunction with casein supply problems have, however, improved the competitive position of starch-based products.

Some cold setting synthetic products have been developed specifically for corrugated board manufacture but at present these adhesives are regarded as a supplement to standard starch adhesives and are mainly recommended for use on the heavy weight, multi-ply boards with double facer glue application, or if the liner board being used is coated (Cerestar product information, Cerestar UK Ltd, Trafford Park, Manchester).

7.6.5 Conclusions

The market for adhesives is of modest importance in terms of the overall UK industrial starch utilisation within which the corrugated paper market dominates. Despite the inroads of synthetics, the use of starch is likely to predominate as there is an appreciation of the reliability of supply, the simplicity of processing for its use and a growing appreciation of the benefits of a natural product. Overall, the market for adhesives is likely to show a modest rise in parallel with the move out of world recession. Although potato starch is used for some products within this sector, e.g. wallpaper adhesives, due to its superior performance, native or simply modified maize starch is used for the bulk of this sector (i.e. corrugated board manufacture). The main obstacle for increasing the use of wheat starch for this is the conservatism of processors who wish to stay with a product they know and one which fulfils their current needs. A growing differential between the cost of maize starch and wheat starch (see Chapter 5) may encourage a reassessment of this view.

7.7 Starch for mineral oil drilling

7.7.1 Starch utilisation

Starch can be used in the oil industry where it functions as a drilling aid. During drilling, drilling fluids in the form of circulating aqueous clay suspensions are used to stabilise the wall of the bore-hole. These fluids enable drilled solids from the drilling bit to be transported to the surface by exerting hydraulic pressure on the wall. Fluid can be lost into the often porous soil formation and so to prevent this, a sealing filter cake is built against the wall. Drilling fluids may be oil- or water-based. Due to their water holding capabilities, starch products are incorporated into water-based drilling fluids to control fluid loss. Starch can be included in a number of different formulations of water-based fluids. In other water-based fluids, polymers derived from guar gum, and cellulose from cotton and wood are used instead of starch. Cellulose ethers may also be used as starch alternatives.

7.7.2 Market size

The amount of drilling fluid used varies substantially with the number of wells in operation. In 1989, for example, 146 000 t of drilling fluid was used in the North Sea Sector, compared to 326 000 t in 1987. It is estimated that 40% of drilling fluids are water-based and of these 5 - 10% contain starch at a concentration of 1 - 3%, indicating a maximum annual market requirement of 400 tonnes based on 1987 drilling figures. This represents just 0.18% of the industrial use of starch in the UK.

7.7.3 Starch type used

To provide the viscosity and water holding capacity required for use in drilling fluids, starch must be modified before use in this application. Since it is not convenient to have starch cooking equipment on an oil-drilling site, the starch is pre-treated to a cold-water soluble (pregelatinised) form. Waxy maize, potato, tapioca and sago are preferred because of their superior viscosity and water holding characteristics. Maize starch does not have the viscosity and water holding qualities required and it seems likely that UK wheat would be similarly disadvantaged. In the UK sector it is estimated that 99% of the starch used in drilling fluids is potato-derived. The starch is often carboxymethylated with a high degree of substitution (see Section 6.2.3).

7.7.4 Potential developments

Increasingly stringent environmental legislation is leading to the replacement of mineral oil drilling fluids with drilling fluids that are more biodegradable.

Research is ongoing to modify starch to increase its suitability for use under a wider range of conditions. Drilling fluids containing concentrations of up to 40 % of a starch derivative in the aqueous phase are under investigation and some patents for this type of product have been lodged. Development of such products could lead to a 20 fold increase in starch use in drilling fluids. The fluids are, however, at an early stage of commercial uptake. This work coincides with research into other biodegradable drilling fluids such as pseudo (synthetic) oils and vegetable oils, which would compete with starch-containing drilling fluids on the market.

There is the likelihood that all drilling fluids used in the future will have to be biodegradable. In the UK at present, all starch-based fluids are biodegradable. Elsewhere, carboxymethylation treatments are used with some fluids which leads to a loss of biodegradability. Biocide is added to some starch drilling fluids to reduce microbial growth prior to use and this leads to slower degradation thereafter.

Starch-containing, water-based fluids are less suitable than mineral oil-based fluids for conditions of high temperature. In the more inaccessible areas where drilling conditions are more demanding and drilling temperatures are higher the use of starch drilling fluids may be limited. With the future development of many wells likely to occur in these less accessible areas the future use of starch containing fluids may be limited. Petrochemical-based drilling fluids have superior technical qualities. However if starch can be modified for high temperature use, it would increase its potential market significantly.

Oil-based fluids cost three times the price of water-based fluids at present, therefore cost will not be the limiting factor for use of starch-containing drilling fluids. The restricted range of conditions in which starch-containing drilling fluids can be used will be the largest limitation for use.

7.7.5 Conclusions

The potential market for starch-based drilling fluids in theNorth Sea is very small. However, current investigations are looking towards much higher starch concentrations within the fluid. This, together with environmental legislation leading to the need for more biodegradable fluids should increase the potential market. However, as oil-based fluids are much more expensive than water-based starch-containing drilling fluids there appears to be sufficient incentive for the oil companies concerned to conduct the near market research required.

7.8 The use of starch in the agrochemical industry

7.8.1 Starch utilisation

Starch use within the agrochemical industry is currently an active area of research. For example, US work has shown an application as an encapsulation agent for pesticides. Starch encapsulation leads to safer handling of pesticides. Efficacy of the active ingredient is also improved with better delivery to the target pest and a reduction of losses that normally occur by evaporation, leaching and light decomposition. In the past, encapsulation using starch was comparatively costly because of the chemicals needed to solubilize and cross-link starch. A new technique using extruders has been developed which eliminates the need for chemical addition. Trials have shown that encapsulation of herbicides significantly reduces the amount of herbicide runoff giving environmental attractions.

In agrochemicals there is also a need for new aqueous-based coatings, such as film-forming polymers which are lipophilic and more water resistant, so that they fall apart fairly slowly and release the active ingredient more slowly. Microcrystalline cellulose performs well and is useful in some applications, but for agricultural chemicals is too expensive. Amylose has good film-forming properties and is similar in structure to cellulose. The development of crops that produce starch high in amylose (as is being carried out by Avebe) may therefore be of interest in this sector.

Pesticide formulations are moving towards aqueous bases. Many of the active ingredients are organics with low aqueous solubility. As a consequence of this, work is ongoing to develop structured suspensions. There is also a need for carriers in solid formulations and thus a need to disperse suspensions in water. The main competitive element here is price. For example, xanthan gum is expensive and often too viscous, particularly at low temperatures. Cyclodextrins[1] perform well in these applications but several molecules are required per molecule of active ingredient and if 1 kg of active ingredient per hectare is required, 7 - 8 kg of cyclodextrin is needed, which, at a price of £10 per kg, is far too expensive.

Within the UK, a starch-based product called Hugtight has been developed by the Humber Growers Association to control downy mildew and pests on cucumber. However it appears to perform less well than established synthetic products. This is due to a reduction of photosynthetic capacity, caused by the high rate of application necessary. Another undesirable effect may be to encourage fungal growth on foliage.

Research results within the agrochemical industry are commercially sensitive and with little coming forward for patenting as yet, the potential application of starch in the agro-chemical industry remains unclear.

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[1] Cyclodextrins are a group of cyclic oligosacharides, composed of 6 - 8 glucose residues, that can be produced enzymically from starch. The necessary enzyme occurs in the bacteria *Bacillus macerans*. Cyclodextrins are useful for preparing aqueous suspensions of organics with low solubility because the cyclodextrin ring can hold hydrophobic molecules (see Chapter 3.3).

7.8.2 Conclusions

At present there are several different areas of research for the use of starch in the agrochemical industry. Were any of these to come to fruition, the potential market could be moderately large in a European context. However, in the case of encapsulation, which appears the most promising in this area, the starch would most likely be modified and used at the site of chemical manufacture. Currently the UK produces only a small portion of the agrochemicals used within Europe and so benefits in this area for the UK appear small.

7.9 Pharmaceuticals

7.9.1 Starch utilisation

This is a sector considered to have potential by starch processors. Starch is used for coating and dusting tablets as well as for binding the materials which make up tablets and as a disintegrating agent. Starch can be used in pharmaceuticals in the same way as it is used in the food industry, to influence or control characteristics such as texture, aesthetics, moisture, consistency and shelf stability. Starch can be used to aid processing, packaging, lubrication or moisture equilibration. Starch and starch derivatives can also be used in the production of active ingredients, by acting as a feedstock for fermentation processes, for the production of materials such as antibiotics, amino acids, organic acids, vitamins, enzymes and hydrocolloids, or as a base for chemical transformation. There is scope both for substituting for existing products and for manufacturing of new products.

7.9.2 Market size

The pharmaceutical market is a relatively low volume market for starch, but potentially high added value where the production of active ingredients is concerned. EU data (see Table 1.1) indicates that the quantity of starch used directly for pharmaceutical manufacture in the UK in 1993/94 was 4 880 t (or 2.3% of total UK industrial starch use), all of which was maize starch. The equivalent figure for the EU (Table 1.2) indicates that a similar proportion of industrial starch is used for pharmaceutical production: 49 110 t (2% of total industrial starch use). It should be noted, however, that the actual quantity of starch used for pharmaceutical production may be higher, as some of the starch accounted for in the category "organic chemicals" may ultimately be used in pharmaceutical production.

7.9.3 Examples of use and starch type used

7.9.3.1 General use. Table 1.1 indicates that all the starch used for pharmaceutical production in the UK is maize starch. In addition any starch used for pharmaceutical production via organic chemical production is also likely to be maize starch. The figures for the EU indicate that 97% of starch used is maize starch with very small quantities of wheat (1.9%) and potato (0.7%) also used. Potato starch may perform better as a tablet disintegrating agent than wheat or maize starch because it has a superior swelling power, and the small quantity of potato starch used within the EU is likely to be used in this way or as a tablet binder or coating, rather than as a feedstock for fermentation processes.

7.9.3.2 Amylose. It was noted some time ago (Langlois and Wagoner, 1967) that amylose and its derivatives have properties that are useful in pharmaceuticals. The opportunities identified for the use of amylose are listed below.

(i) The good film-forming properties of amylose make it particularly suitable for coating tablets.

(ii) Because amylose is free-flowing, self-lubricating and self-disintegrating, it can function as the filler, lubricant and disintegrant as well as the binder in tablets.

(iii) Amylose has been proposed for use as an active ingredient of pharmaceuticals. The use of sulphated amylose to preserve the mucosity of the stomach by inhibiting pepsin activity has been described in a patent.

Although it is not clear how these reports relate to practice in the pharmaceutical industry today, they suggest that there may be an opportunity for high amylose starch (e.g. from potatoes, see Chapter 3) in the pharmaceuticals industry.

7.9.3.3 Dextrose. Dextrose is is made by the crystallisation of concentrated glucose syrups, which in turn may be produced from starch. Maize starch is most often used for this purpose. Dextrose is used in making tableted products in both the food and pharmaceutical industries. In a highly purified state, dextrose is used in medicine for oral and intravenous feeding (Röper, 1993; Cerestar product information, 1994; Kooi and Armbruster, 1967).

7.9.3.4 Hydrolysis and fermentation products. In the U.S., citric acid has been produced from both petroleum and agricultural feedstocks. Recently, there has been a shift towards production from agricultural feedstock, which utilises a special microbial strain of *Aspergillus niger* to ferment crude sugars or maize starch in the presence of oxygen. Although maize is principally used in the U.S., the sugar feedstock can be derived from any starch-rich crop, including wheat or barley. Citric acid is the main acidulant (by volume) used by the food and pharmaceutical industries (in the U.S.). Use of citric acid by the pharmaceutical and cosmetic industries in the U.S. accounts for 7% of total production. Citric acid is used in a variety of drugs including the manufacture of citrates and effervescent salts. Total U.S domestic consumption of citric acid was estimated as 360 million pounds weight in 1994. Production of this quantity requires approximately 16 - 18 million bushels of maize.

Sorbitol (see Figure 6.1) is used as the starting material for vitamin C synthesis.

Dianhydrosorbitol and dianhydromannitol (see Figure 6.1) are used for the manufacture of dinitrates which are used as vasodilators for the treatment of coronary diseases and angina pectoris.

7.9.3.5 Carboxymethyl starch. Research has indicated that these modified starches (see Section 6.2.1) are suitable for a range of different medical applications such as anions in salts of certain drugs and disintegrants. They have also been investigated for use as an active ingredient. Carboxymethyl starch or amylose have been injected into mice, resulting in a 50% reduction of malignant tumors. Carboxymethyl starch has been proposed for use in medical poultices and dentifrice powders (Hofreiter, 1986). When antibiotics, some alkaloids, local anaesthetics, basic cytostatics, antihistamines, and some other drugs, are used in the form of their salts with carboxymethylamylose or sulphonated amylose, their ability to enter the lymphatic system has been reported to increase (Langlois and Wagoner, 1967).

7.9.3.6 Starch phosphate. Plasticized starch phosphate films have been found to be useful in treating skin wounds. Rapid healing, less infection, more rapid tissue growth and less interference with the natural healing process were claimed (Solarek 1986).

7.9.3.7 Chiral carbohydrate building blocks. An area of potential interest is the production of chiral carbohydrate building blocks for use as intermediates for pharmaceutical synthesis (Röper, 1993). Starch can be hydrolysed to produce D-glucose which is fermented into a mixture of Ribitol, erythritol and glycerol which can be separated. Ribitol and erythritol are transformed into L-ribulose and L-erythrulose by enzymatic transformation. L-Erythrulose shows potential as an intermediate for the synthesis of biologically active compounds and can also be transformed into L-glyceraldehyde, an important chiral C-3 building block for the synthesis of beta-blockers, platelet activating factors, prostaglandins or leucotrienes.

7.9.4 Factors limiting development

A major European starch processor considered that the cost of adhering to EU regulations was a major limitation on the development of starch for the manufacture of pharmaceuticals. However, this is not a problem specific to starch; it affects all types of pharmaceutical products. Some toxicity testing is required if more than 10 kg of a new product is introduced to the market place. If the quantity is more than one tonne, full toxicity testing is required. It can cost £1/4 million simply for registration of a product. The legislation means that companies have to fully evaluate the market at a very early stage of development, in order to decide to make the investment. This required investment may limit development of this sector.

7.9.5 Conclusions

Pharmaceuticals cover a vast spread of products - many of which incorporate starch derivatives, either as a basic ingredient or as process intermediates. Current research and development in this sector is commercially sensitive, and it is therefore difficult to assess how the reports in the literature described above relate to current R & D within the industry or current manufacturing practice. However, some starch processors consider this to be a promising sector, and published research indicates potential for continuing development of starch-based products. This is a low volume market, so any developments are unlikely to have a great impact on UK agriculture. There may be a niche for high amylose starches in this sector (see Chapter 3), but again quantities required are likely to be small. The main interest from the starch processors point of view is the opportunity to develop "added value" products and the main opportunity for this may lie in research activity within the starch industry to develop active ingredients based on the structure of starch. However, this is a high investment, high risk business. Other routes to the production of added value products lie in the continued production and development of modified starches and starch derivatives as intermediates for use by the pharmaceutical industry.

7.10 Cosmetics and toiletries

7.10.1 Starch utilisation

Starch and starch derivatives have a wide range of potential applications in the cosmetics and toiletries industry. Toothpastes, shampoos, permanent waves, stick deodorants, soaps, shaving and other foam creams, room deodorisers, hair gel and perfumes are all products which could potentially include starch and starch derivatives. However, an EEC study (Anon, 1986) found that, in practice, starch and starch derivatives were included in a much smaller range of products. The limited use of starch was attributed to factors such as cost, technical suitability, consumer acceptance and traditional industry practice. However, starch processors currently consider the cosmetics and toiletries sector to be an area with good potential for development, as a low - moderate volume but high added value sector.

7.10.2 Examples of use and starch type used

7.10.2.1 Sorbitol. An established use of starch in the toiletries sector is the use of sorbitol in toothpaste. A general scheme for the manufacture of sorbitol from starch is given in figure 7.10.1.

Starch
|
(*enzymic conversion*)
↓
maltodextrins
|
(*enzymic conversion*)
↓
glucose
|
(*chemical conversion*)
↓
sorbitol

Figure 7.10.1 General scheme for the production of sorbitol from starch

Sorbitol is commonly added to toothpaste to keep the paste moist. It came into wide usage because it was cheaper than its main competitor, glycerol, which appears to perform better. Sorbitol is also used in many creams such as handcreams, body lotions and make-up foundations. In creams and lotions the proportion of sorbitol might typically be 5% of solids added, but 10 - 15 % of the value of inputs. Sorbitol and sorbitol derivatives are also used in other cosmetic products, for example as part of the colour dispersal system in colour cosmetic products. Small amounts of sorbitol may also be incorporated into some shampoos (Anon, 1986; Cerestar product information).

7.10.2.2 Cross-linked starches. Cross-linked starch (see Section 6.2.1.3) has been used in the granular form in antiperspirant sprays. Combination treatments involving cross-linking potato starch with epichlorohydrin and etherifying with monochloroacetic acid have been used to prepare absorbents for disposable sanitary products (Wurzburg, 1986).

7.10.2.3 Starch graft co-polymers. A starch graft co-polymer is a synthetic polymer (vinyl or acrylic) grafted to starch. Graft co-polymers are prepared by first generating free radicals on starch and then allowing these free - radicals to serve as macroinitiators for the vinyl or acrylic monomer. If starch-grafted polyacrylonitrile is treated with either sodium hydroxide or potassium hydroxide solutions at temperatures near 100°C, nitrile substituents of PAN are converted to a mixture of carboxamide and alkali metal carboxylate, and ammonia is evolved. Carboxamide to carboxylate ratios will vary depending on saponification conditions, but are typically in the order of 1:2. An important application of saponified starch graft co-polymers with polyacrylonitrile (HSPAN) is in disposable soft goods designed to absorb body fluids such as adult incontinence pads, nappies, hospital underpads and feminine sanitary products. Research has been directed towards improving the rate of absorption, and both surface treatment of HSPAN with polyethers and addition of fumed silica or alumina to HSPAN have been patented. In addition, HSPAN has been marketed for addition to colostomy and urinal bags to prevent leaks and odours. The advantage of HSPAN over cellulose products is reduced bulk with equal or superior absorbancy. HSPAN has also been used as a perspiration absorbant in body powder formulations (Fanta and Doane, 1986).

7.10.2.4 Starch derivatives of substituted dicarboxylic acids. Starch derivatives of substituted dicarboxylic acids in the granular form can be readily suspended in water, just like their base starches. However, when these derivatives are further treated with a polyvalent metal or alkaline earth metal ion and dried, they possess two unusual properties: excellent free flow and water repellency. Unlike ordinary starch, the free- flowing water-repellent derivatives disperse well in organic solvents, do not clump and give a smoother silkier feel. This is the reason why these products are often used in oil- or petroleum-based cosmetic pastes as opacifying agents and texturisers. Free-flowing water-repellent maize starch is used in alcohol-based lotions and body deodorant sprays which, on drying, leave a silky film on the skin. Another application is in body powders, in some cases replacing talc. The ability of hydrophobic starch to absorb excessive moisture gives the body more lasting comfort (Trubiano, 1986).

7.10.2.5 Carboxymethyl starch. Use of carboxymethyl starch in dental powders has been proposed (Hofreiter, 1986).

7.10.2.6 Cationic starches. Hydroxyalkylated, quaternary ammonium starch ethers were combined with various ingredients to make hair shampoo. Tertiary amino alkyl high amylose (>50%) starches were suggested for hair-holding compositions (Solarek, 1986).

7.10.2.7 Carbohydrate-based emulsifiers. Cerestar has patented a process to manufacture butylglucoside esters, targeted for use in cosmetic formulations, using an enzyme-catalysed esterification of *n*-butylglucoside (derived from starch by a series of enzymatic and chemical processes). The advantages of this enzymatic process are:

(i) the low reaction temperature avoids colour formation
(ii) high reaction specificity leads to defined tailormade products
(iii) the enzyme catalyst is natural and non-toxic
(iv) the product is free from organic solvents and toxic contaminants
(v) the product is not an irritant
(vi) the product is biodegradable
(Röper, 1993)

7.10.2.8 Ethanol. A large number of cosmetic products (for example, perfumes and hairsprays) are based on ethanol or contain ethanol. Ethanol for industrial use can be produced from starch by fermentation (ethanol produced in this way is often termed bioethanol) , but can also be produced by the petrochemical industry (ethanol produced from the petrochemical industry is termed synthetic ethanol). Bioethanol produced in the UK from wheat could not currently compete with synthetic ethanol on price (Batchelor *et al.*,1994), but may be attractive to some cosmetics manufacturers, at the upper end of the market, where a natural image is used as a marketing tool.

7.10.2.9 Talcum powder replacement. Maize starch can be used to replace talc in baby, body, face and foot powders, due to its absorbent properties (Cerestar product information). Other starches may be particularly useful in this sector. A Canadian company, Canamino, has developed the use of oat starch as a talcum powder replacement. The starch is surface-treated to flow and feel like talcum powder, and can be used where the safety of talcum powder has been questioned. Quinoa is also being considered for use in paper-coating and the production of dusting powders and cosmetics (Fleming and Galwey, 1995).

7.10.3 Conclusions

Cosmetics and toiletries cover a wide range of differing products. This is a low - moderate volume/high value market sector so developments are likely to have a positive benefit to both agriculture and the industrial sector. The main areas for research lie in product development which is currently conducted by the private sector. There is relatively strong interest from starch processors who see an opportunity to develop "added value". An intensified use of low molecular weight carbohydrates as raw materials for the cosmetics industry is expected, so cereal starches are in a position to fulfill this opportunity. This sector would benefit from fuller exploration of the potential for oat and quinoa starch.

CHAPTER 8 THE DEVELOPMENT OF THE UK INDUSTRIAL STARCH INDUSTRY

Within the EU, the balance of industrial starch use from potatoes, maize and wheat is shifting in the direction of cereals. This is principally price-driven with processors progressively prepared to accept some short-comings of the cereal product where this allows them to secure a cheaper raw material. The potato starch supply shortages of 1995 (and probably 1996) have played (and will play) their part in this move. However the particular characteristics of potato starch (e.g. large granule size, high phosphorus content) will ensure that certain industrial sectors, e.g. flocculants, will always show a strong preference for potato starch. The development of low and high amylose potatoes may strengthen some and develop new industrial markets so potentially redressing the balance in industrial starch use.

Quota restrictions on the allocation of EU support payments to potato starch manufacturers currently prevent any development of a UK potato starch industry. The price assumptions and margin calculations set out in Section 5.3, show that the commercial attraction of potato starch manufacture is poor and highly dependent on the payment of the special "fixed premium".

Despite the relatively high potato yields regularly achieved in Britain, UK potato growers will not find it attractive to grow starch potatoes for industrial markets at £40.00-45.00/tonne without EU compensation - the prescribed 1995/96 minimum price for starch potatoes within the EU. Potato starch processors are unlikely to pay above this level if they are to obtain a positive margin from starch manufacture (see Section 5.3). Elsewhere in the EU, starch potato growers receive compensation for these low prices in relation to starch yield. In 1995/96, potato starch growers will be eligible for compensation payments of 85.81 ECU/tonne of starch. A typical starch content of 20% of the "under-water weight" will give growers compensation payments of 19.95 ECU/tonne of potatoes delivered to factory (£16.83/tonne @ the green pound rate of 4/7/95). This gives a total return of approximately £56 - 62/tonne. These compensation payments are however unlikely to be available to UK growers due to EU quota restrictions on potato starch support payments.

Potato gross margin calculations show a crop yielding 40 tonnes/ha will give a gross margin of approximately £1 808/ha when ware potatoes are sold at £85/tonne (Table 8.1). A potato starch price of £45.00/tonne without EU compensation would reduce gross margins to below £400/ha . Growers are unlikely to find this attractive given the alternative of a set-aside payment of around £300 - 350/ha and the additional management effort required to grow potatoes. UK growers would not find it attractive to grow starch potatoes for industrial purposes on set-aside land. Set-aside payments are not paid when crops that attract a production refund are grown. Without this payment gross margins would remain below £400/ha. UK growers would also need to overcome any reluctance of the established starch potato industry to supply high starch content potato seed to a competing industry. Transport costs will prevent any commercial movement of UK starch potatoes to established processors elsewhere in the EU.

The survival of the Dutch potato starch industry has been dependent on the concentration of potato starch production in very large processing facilities where economies of scale have been maximised and where effluent problems could be tackled efficiently. In parallel with this, the intensity of Dutch agriculture (where potatoes are grown in extremely short rotations using soil sterilants) has allowed large scale potato supply within a locality which is required to maintain factory throughput without excessive transport costs. These developments have been essential to allow the Dutch potato starch industry to compete effectively with other starches and even so, EU support is required. The introduction of such an industry to the UK would not be without its problems and could affect the stability of the existing seed and ware industry within the UK.

Assuming that the UK does not secure any EU potato starch quota then any development of the UK industrial starch industry will need to concentrate on opportunities presented by cereals - particularly wheat starch. Maize starch manufacture remains dependent upon imported maize and was shown to be commercially somewhat less attractive relative to wheat. Wheat is widely available and profitably grown within the UK, although current regulations (EC Commission Regulation 1722/93) **exclude** cereal growing for starch from set-aside land. A comparison of processing margins in Sections 5.3 - 5.5 showed wheat starch manufacture to be superior to both maize and potato. An expansion in wheat starch manufacture, either by the conversion of existing plant or the establishment of new capacity within the industry, would potentially allow:

(i) the replacement of starch imports (potato, maize and wheat) currently running at around 130 000 tonnes p.a.
(ii) the substitution of maize starch - both imported and domestically produced, in industrial markets
(iii) a contribution to normal UK wheat gluten requirements estimated at 52 000 tonnes p.a. of which approximately 17 000 tonnes are imported.

A wheat starch plant with a processing capacity of approximately 100 000 tonnes, would produce 46,000 tonnes of native wheat starch and approximately 9 000 tonnes of wheat gluten. This is almost one third of the UK's annual wheat gluten imports of 30 000 tonnes.

The move to duties on cereal imports from 1/7/95, as part of the GATT agreement, is not expected to change the competitive position of wheat in the UK relative to maize and potatoes. EU cereal growers will continue to receive considerable protection from third-country imports. Import prices are forecast to be 155% of the intervention price after the imposition of fixed tariffs. Export refunds will still apply to food items included within the CAP. Industrial starches, as now, will trade with no external trade support but with production refunds unchanged by GATT. These refunds will only fall as maize intervention prices fall. Wheat starch manufacturing economics, however, may be damaged by a reduction in wheat gluten values should imported quality milling wheats become more competitively priced in the UK as a result of GATT duty restrictions. Any increase in breadmaking wheat imports will reduce gluten demand, (and price levels) for fortifying home-grown wheats of lower quality. The overall attractiveness of wheat starch would be improved through the development of better protein separation at milling.

There are relatively major gaps in the knowledge of starch production and its industrial potential which range from a cellular to a whole crop agronomic level. For example, further work is required to elucidate the precise role and relative importance of starch synthesis and the starch synthase enzymes. These enzymes control both the amount and organisation of amylose and amylopectin and hence dictate the quantity and industrial use of the starch produced. A more comprehensive knowledge of starch synthesis would allow a more directed approach to varietal improvement through genetic modification.

At the whole crop level, there are indications that growing location and crop management may significantly influence industrial starch characteristics. Currently there is no indication whether all or parts of the UK offer particular advantages for industrial starch production, and no management information to indicate how potential benefits could be maximised, yet this potentially offers a relatively inexpensive method of achieving improved industrial characteristics and improving the UK's competitive position within the European starch industry.

Both quinoa and oats merit more detailed work to assess their industrial potential. Oats yield as well as the other major cereals in certain locations and the UK is better placed than our EU competitors for high oat yields. A further exploration of potential industrial markets is merited.

Of all the industrial sectors examined, detergents, particularly surfactants, offer the largest potential new market. As the product is not influenced by native starch properties, the selection of starch source is very much price-driven thus opening up the opportunity for UK-produced cereal starch. Many companies are active in R & D in this area but this work is highly confidential.

Government funded research to benefit this area would be most appropriately directed towards research of a fundamental nature which would encourage price competitivity of UK-grown crops. A tightening up of the enforcement of European legislation on biodegradable surfactant use would accelerate developments in this area.

Table 8.1 Potato production gross margins 1995/96

		Ware Potatoes	Starch Potatoes	
Yield: t/ha:	Sold	36	36	
	Stock feed	4	4	
			Compensation	
			with	without
Output:		**(£)**	**(£)**	**(£)**
	Ware @ £85/t	3 060.00		
	Starch @ £45/t		1 620.00	1 620.00
	Stock feed @ £15/T	60.00	60.00	60.00
	Starch compensation (1)		606.00	
		3 120.00	2 286.00	1 680.00
Variable costs (£/ha)				
(seed, fertiliser, agrochemicals, contractors)		1 312.00	1 312.00	1 312.00
Gross margin (£/ha)		1 808.00	974.00	368.00

Source: SAC Farm Management Handbook 1994/95.

(1) 1995/96 compensation at 85.8 ECU/tonne of starch
at 19.95 ECU/tonne of starch potato (20% starch)
is equivalent to £16.83/tonne (4/7/95)
or £606/ha at 36 t/ha sold

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Appendix 1

Gelatinisation and **pasting** are the processes involved in the formation of a starch paste. These processes are essential for industrial uses where starch is used in the form of a paste; they alter rheology and viscosity properties of the system that the starch is in.

Starch granules are insoluble in cold water but do absorb water to a limited extent when suspended in water or exposed to high humidity, but the swelling is reversible and the crystalline structure of the starch is essentially retained. When a slurry of starch is heated above a critical temperature (the **gelatinisation temperature**) which varies between different starch types, the hydrogen bonds responsible for the structural integrity of the granule weaken, allowing water to penetrate and hydrate the linear segments of the amylopectin. As this occurs the molecules start to form helices or coils, creating tangential pressures which cause the granules to take water and swell to many times their original volume. During this irreversible swelling the amylose tends to leach out of the granule and, along with the amylopectin, becomes highly hydrated. The suspension begins to clarify and its viscosity increases. The temperature at which the viscosity increases is the **pasting temperature**. The viscosity of the suspension increases until it reaches a peak viscosity where the granules have approached their maximum hydration.

The industry tends to use the term "solution" to describe starch pastes, or other mixtures (e.g. suspensions) of starch and water, which are not always strictly speaking solutions. Small, short- chain length starch molecules will actually enter into solution as a result of the gelatinisation and pasting processes. Larger molecules can also enter into solution but are far less stable and tend to retrograde. **Retrogradation** is the return of dissolved starch molecules to a more orderly state (as a result of hydrogen bonding) which is different from the original state of the starch granule and is usually considered undesirable. Retrogradation results in precipitation of the starch from the solution. Starches from different sources vary in their tendency to retrograde.

A starch paste may therefore be a solution, but it often may consist of a starch solution with starch suspended in it. The extent to which starch forms a real solution is determined by a number of factors including the characteristics of the starch (e.g. chain length), the concentration of the starch and the temperature of the whole mixture. In general, native starch has to be modified to some extent in order to form a true stable solution, for example, chain length may be reduced by acid hydrolysis.

Appendix 2

Phytoglycogen is similar to amylopectin since it is composed exclusively of D-glucopyranose residues. It is also composed of short α(1-4) linked chains which, at their reducing termini, are then linked by α(1-6) linkages to another chain of α(1-4) linked residues. The trichitic type structure of amylopectin is retained. The difference between amylopectin and phytoglycogen is that there are more α(1-6) linkages in phytoglycogen, which makes it more highly branched. The average chain lengths of the α(1-4) linked chains are therefore 10-14 in phytoglycogen, whereas they are 20-25 in amylopectin. The value of 10-14 is similar to that found in mammalian glycogen.

The presence of phytoglycogen is easily recognised from the spectrum of its complex with iodine. That from amylopectin is purple with a λ_{max} of 530-550 nm while the λ_{max} of that from phytoglycogen is at 430-450 nm and is brown. The genetic reasons for the production of phytoglycogen as opposed to amylopectin are still not confirmed but the sugary (*su*) mutants have much lower levels of the α(1-6) debranching enzyme. The major practical difference is that phytoglycogen is water soluble while amylopectin is not readily soluble in water.

Appendix 3

There is considerable interest in and need for the production of cationic and anionic starch derivatives. These are chemically produced by introducing substituents such as diethylaminoethyl or carboxymethyl groups respectively. These substituents are usually introduced at C-6 of some of the glucose residues to allow the ion exchange facility to be used. As well as these synthetic derivatives of glucose, there are natural derivatives which have inherent chemical groups which allow them to act as ion exchange resins. D-glucosamine is a natural product, being found in many sources but particularly as the main component of a polysaccharide, chitosan, from the *Crustaceae*. The amino group replaces the conventional hydroxyl group at C-2 of the glucose structure and the polymer will form amine salts with anions. As well as the free amino group, many of the natural sources of glucosamine contain the N-acetyl group, but this will also act as an ion exchange resin although its reactivity is different to that of the free amino group. Polymers containing almost exclusively the N-acetyl group are called chitin.

Being a natural sugar, the genes for D-glucosamine synthesis will eventually be identified, sequenced and cloned. It may then be possible to introduce these genes into plants and make them produce these materials.

The corresponding cation exchange resins could be produced by genetic engineering to introduce glucuronic acid into the "starch" in place of glucose. The chemistry of glucuronic acid is more complex, since it readily forms an anhydride and, to the best of our knowledge, no homoglucuronic acid polysaccharide has been identified. It is normally found in the plant kingdom as a single constituent of polysaccharides. However, since it is found, biosynthetic enzymes must be present and it is possible that this sugar could be introduced into a "starch" in the future. It should be noted that the corresponding derivative of the sugar galactose, namely galacturonic acid is also found and is the major constituent of pectins.