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Starch in Paper Industry

INTRODUCTION

Addition of starch has been recognised from the early days of paper making as being capable of imparting desirable physical properties. It has been reported that the Chinese paper makers employed this substance about 700 AD. Today in U.S. and Europe, paper industry is the largest non food outlet for starch. Its popularity is strikingly manifest in the fact that the volume of starch consumed by the paper industry three and a half times that consumed a decade ago.

THE STARCH INDUSTRY

a) General :

Starch is one of the earth's plentiful materials and is produced in abundance by vegetable life. It is a reservoir of energy for all plants. The starch industry in India had its origin during the 2nd World War, when supplies of starch to the Indian textile industry were cut off as a reason of German blockade. The textile was a high priority industry then and was considered essential for war effort. The beginning was modest mostly using simple methods and devices. But in due course, modern technology and equipment have come into use and today this industry can reasonably boast of high efficiency and quality equal to imported products. The Indian starch industry mainly uses indigenous maize and tapioca as raw-materials and has an installed capacity for 1,50,000 tons maize starch and 200,000 tons tapioca starch. The industry meets the entire domestic requirements of starch and has a surplus capacity to meet the target of the 4th National Plan and further some exports. Unlike in the paper industry, the capacity utilisation in starch industry is only 50%.

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b) What is Starch ?

Starch is a white granular substance, insoluble in cold water, alcohol and most other solvents. When cooked with water, it forms a viscous solution. When lightly stained with dilute iodine solution starch gives a characteristic blue or reddish coloration and this is used as specific test for its identification. A naked eye can detect no difference among refined starches. Each starch has its individual personality and microscope reveals uncooked starch to be composed of tiny cells "granules".

When an aqueous suspension of starch (say 1 part with 15 parts water) is heated beyond a critical temperature (gelatinising temp.) the granules tend to swell. On continued heating, they form viscous paste. On cooling, the paste increase in consistency, This is known as "pasting or cooking curve". Some starches jel, others form soft pastes. The starch pastes differ in clarity. Some are clear and others are cloudy to opaque. The difference depends on the botanical variety. Table I sums up the physical properties of the two main commercial starches produced in India.

TABLE I

PHYSICAL PROPERTIES OF STARCHES

Starch	Cell size microns	Temp. °C of gelatinisation 5% solution	Starch paste Texture	Starch paste Clarity
Maize	10-25	80	Jel	Opaque
Tapioca	10-35	74	Cohesive	Clear

whose size and shape are characteristic of each botanical variety. All starches can be converted (hydrolysed) in the presence of acids to form dextrose.

c) Starch Properties :

The understanding of the properties of starch is essential for its utilisation in order to derive the maximum benefit. Like the high polymer cellulose, starch is a combination of carbon, hydrogen and oxygen atoms arranged as chains of glucose residues, in large molecular aggregates. Starch has two different types of polymers. These are straight chained or linear amylose molecules and branched amylo-pectin molecules. The granules of all starches contain both types molecules, but in different proportions. The amylose molecules contribute to the jellying characteristics found in cooked and cooled starch solution. Amylo-pectin molecules impart the gummy or cohesive and tacky properties.

It will be observed that maize starch gelatinises at a higher temperature than tapioca starch. Further its paste, is more resistant to viscosity, on continued heating and agitation. The paste from maize starch is opaque whereas tapioca starch paste is clear. One cooling maize starch paste sets to a jet but tapioca starch paste forms a soft paste. The tendency of the starch paste to thicken or jel on cooling or on ageing explains the associative tendency of starch molecules for each other. In some instances this associations between starch molecules progress to the point where it becomes irreversible under normal conditions and some starch may actually precipitate. This molecular association is termed "retrogradation". These properties have a great impact on the end use of starch.

d) Mode of Manufacture :

The two commercially important starches produced in India are derived from maize and tapioca. The methods employed for starch extraction are based on the components of the raw material but these methods follow the same pattern.

d i) Maize Starch

The process has to take into consideration the components of the maize kernel.

TABLE II
CONSTITUTENTS OF MAIZE KERNEL

	%
Moisture	12
Starch	61
Protein	9.0
Oil	3.5
Fibrous matter	9.5
Solubles	5
	100

The process itself is so integrated as to make it an orderly and continuous operation.

Cleaned maize grain is steeped for about 50 hrs. in large cylindrical tanks in warm water slightly acidified with sulphur dioxide. The warm sulphurous acid prevents fermentation, dissolves soluble matter and further facilitates separation of the various components. The steep liquid consisting of solubles is drawn off and concentrated in vacuum evaporators to form steep liquor concentrate (SLC). This SLC is a nutrient in the production of penicillin and other fermentation products and is also used combined with other by-products of maize viz. gluten and fibre to make cattle feeds.

The steeped grain is then run with water in "degerminating mills", where it is coarsely ground to crack and tear and then fed into large vats known as "germ separators". The germ containing oil being lighter than the rest of the grain floats and is skimmed off. The germ is then washed and dried and the oil and oil cake recovered from it. The oil is the most valuable of the by-products and is used in soap making, but in U.S. and other western countries, it is refined to make edible oil. The oil cake is an ingredient for making balanced live-stock feeds.

The balance of the kernel, which sinks to the bottom of the trough is run into special grinding mills called "Buhr Mills' and the resulting slurry is pumped into the DSM System, where fibrous matter is separated from starch-gluten suspension and washed. The fibrous matter is again an ingredient in livestock feeds.

The starch-gluten suspension, until a few years ago was passed over "starch tables" which are long and slightly inclined wooden troughs. The starch being heavier settled out in solid cake and the lighter gluten flowed over. The modern method is to pass the suspension in a series of centrifugal separators, where the centrifugal force separates out the heavier starch from lighten gluten. The latter flows out at the centre and the starch at the periphery. The centrifuge has several advantages over the old starch tables. It gives better separation and since it is enclosed, produces cleaner starch. The starch stream is washed several times to remove remaining impurities and then dewatered, dried and packed or given further treatment to produce converted and speciality starches. The gluten is concentrated by centrifugal force and dried. It is important constituent of balanced live-stock feeds.

d ii) Tapioca Starch :

This starch is produced from topioca tubers cultivated in Kerala and some parts of Tamil Nadu. The starch extraction method is very similar to that for potato starch in Holland. The average analysis of the tuber is as below :—

TABLE IV
ANALYSIS OF TAPIOCA TUBER

	%
Water	68
Starch	26
Fibre	2
Solubles	3
Protein	1

The root is washed and scrubbed. The clean root is then scrapped or rasped to a semi-liquid pulp. Water is then added to the pulp to make a thin slurry. The slurry is then passed through a series of shaking screens or hydraclones to remove fibre and coarse fragments. The liquid suspension containing starch is passed through a series of centrifugal separators to remove soluble impurities and gluten. The starch milk is then centrifuged to remove water, dried and packed or utilised for making derivatives. The spent pulp, which is the only byproduct of some value is used in live-stock feeding.

d iii) Laboratory in Starch Industry :

The operation of the complex processes particularly in the manufacture of maize starch requires prompt and accurate control through laboratory analysis every hour of every day. Laboratories and single purpose testing stations have to be maintained at strategic points in the plant. Incoming raw materials and chemicals have to be analysed. Intermediate steps must be promptly and accurately tested to ensure that operating specifications are met. Finished products must be carefully analysed to make sure that they meet the diverse requirements for their efficient use for different applications. Further the industry has to maintain a programme of applied research in chemistry and chemical engineering. The programme embraces quality control, process efficiency, new products, technical service to customers . This balanced programme ensures high quality and uniformity of starch and starch products.

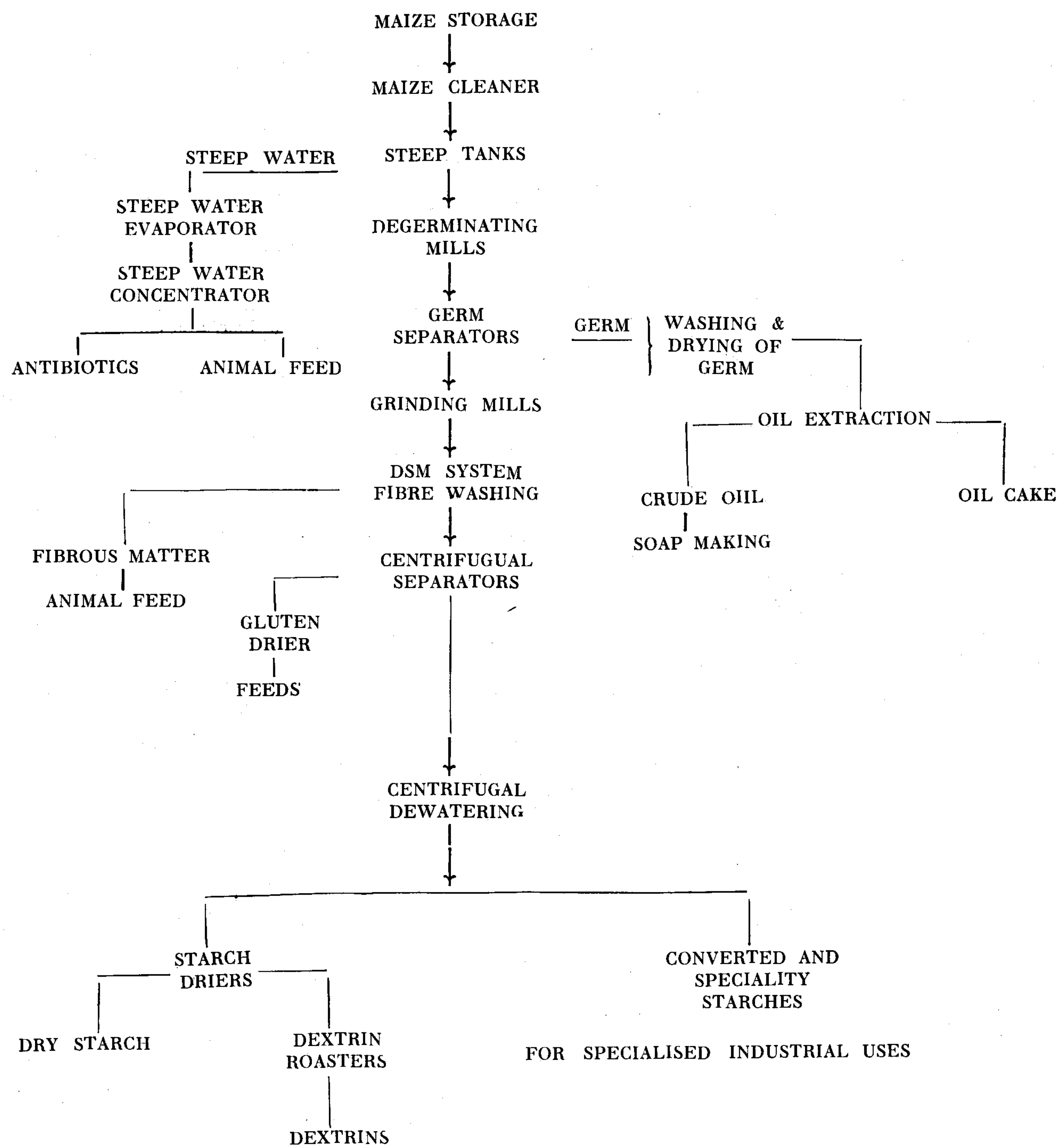
ROLE OF STARCH IN PAPER MANUFACTURE

a) General :

The paper making consists of making fibrous form of cellulose called "Pulp". The pulp is beaten or refined mechanically in water suspension to a state of division suitable for deposition as a thin web, squeezed and dried. Rosin size, alum and dye may be incorporated in the pulp during beating. Other subst-

PROCESS FLOW

TABLE III



ances too are added to enhance paper quality, smoothen the paper manufacturing operation and furnish special properties. Starch and starch products are foremost among them. The increase in consumption of starch and starch products in America and Europe illustrates the point. U.S. alone used 2,00,000 tons of starch in 1965 for 40 million tons of paper produced.

Starch is used in the paper industry in three phase of its manufacture :

i) wet-end additive before sheet is formed

ii) surface sizing including size press and calender sizing and

iii) surface coating as binding agent for clay pigments.

b) Wet-end Additive

In the beaters, the pulp is disintegrated and dispersed into relatively large amount of water by mechanical action. The object is to separate individual fibres and expose greater surface area, which makes possible bonding between fibres, imparting strength. When the disintegration is carried to the extreme by intensive beating or refining, it gives rise to problems. The web does not part with water freely, and paper quality is affected in respect of capacity, compressibility and oil-ink receptivity. The capacity of paper machine being directly related to its ability to get rid of water at the squeezing rolls and drying cylinders, the extra water retained by the highly fibrillated fibres is objectionable.

It is appreciated that a good sheet cannot be obtained by resort to beating or refining alone. This shortcoming however can be overcome by the use of starch as wet end additive. The primary function of starch addition is to increase paper strength, lay down fuzz and increase stiffness and rattle. Conversely, the use of starch permits use of higher ratio of short fibred stock or waste paper in pulp without reducing the strength of the finished sheet. The saving in the expensive type of pulp should be of particular interest to the Indian paper industry, which is short of good quality raw-material for pulp. Starch is used as wet-end additive in three forms :

i) raw starch

ii) cooked starch

iii) speciality products.

Raw starch has been added to beaters, under the belief that if gelatinised, it would filter through on the "wire" with the water phase and not retained by the pulp and also that the heat in the drying cylinder would gelatinize starch. Raw starch however has little absorptive affinity for paper stock and only about 30% is retained by the enmeshment of the web. Even this retained starch is poorly distributed and only a fraction of starch retained is gelatinised. The poor dispersion of starch suffers from the danger of forming "shiners".

When cooked starch is added to beaters, as a reason of colloidal dispersion, the absorbed starch paste will spread over greater area, bringing about a bond between adjacent fibres. The difference between uncooked and cooked starch is that, whereas raw starch is resistant to mechanical treatment (in beaters and refiners) gelatinised starch is unstable. As a result, cooked starch may break down and solubilised to such an extent that much is lost at the "wire".

It will be observed that a suitable starch is one, which is colloidally dispersed sufficiently to enable it to bond the individual fibres and yet is not degraded to the extent that its normal adhesive strength is low or that it has become so degraded (as to become water soluble) as not to be retained by the fibres, but will passout with water phase on the "wire". Considerable research has been directed towards achieving an optimum balance between those factors. As a consequence, starch has been used in the beater in a great variety of forms. Ready to use starch derivatives are now available, which swell and disperse readily in water and are further uniformly dispersed and retained in the web. Further starch should be added at a point where it permits good distribution in the web, without undue degradation of the starch granule. Further starch should be added to the beater after the rosin size but before alum.

Claims made for the effects of starch used in beaters are :

i) permits reduction in beating time and forming a good web.

ii) inproved strength properties, smooth surface with reduced fuzz and good rattle.

iii) beneficial effect in precipitating rosin size uniformly and further acting as an extender to rosin.

iv) permits use of inorganic fillers without sacrificing the critical strength of the finished sheet.

v) permits use of higher ratio of short fibred stock or waste paper in the pulp.

The relationship between starch and cellulose fibre has been explained in terms of "spot welding" theory. The starch is effective only when bridging a gap and creating "fibre-starch-fibre" bond. This suggests that in loosely constructed sheet large swollen granules of starch successfully bridge the gap; whereas in the high density fine grades more dispersed starch brings about bonding. Another salient feature is that, though starch does not directly contribute to sizing as understood by paper technologists, its unique ability to improve this function by causing alum to precipitate rosin size in a more finely divided state and homogeneous distribution over a wider surface is now recognised. The sizing value is said to improve by as much as 25%.

With both rosin and paraffin wax becoming scarcer and costlier, the value of starch as an extender to rosin (as above) calls for further exploration. Another method for economy of rosin is that of H. Wrede, who used soluble silicate in conjunction with starch as a sizing agent for paper. This has been referred to "mineral sizing". Silicate, starch complex, which can be used as complementary to rosin size has been manufactured.

Surface Sizing :

While stock sizing is a process in which paper pulp is treated to impart certain desired properties, surface sizing is a treatment of the near dry or dried paper, to further enhance such properties as resistance to printing inks-oils, varnishes, improve appearance and erasibility or impart other special characteristics.

Surface sizing is generally carried out on the size press. The web of paper before it is thoroughly dried (moisture content should be below 15%) is passed through a size solution, squeezed and then dried. The starch pick-up in the finished sheet depends upon various factors ·

i) degree of sizing and density of untreated base paper.

ii) time of contact between paper and size.

iii) concentration of solution and temperature of application.

iv) pressure at the squeeze rolls.

v) rate and temp. of drying of finished shed sheet.

Considerable development work has been expended in determining the requisite properties for an ideal starch for size press application.

These are :—

i) greatest reduction in viscosity for the least reduction in the molecular size of starch. It should be noticed that too low a viscosity would impair surface finish, whilst too high a viscosity would not allow sufficient penetration.

ii) good stability and controlled retrogradation. Thixotropic set back if present to a limited extent will result in better scuff laying property and produce a more closed **sheet.**

iii) minimum change in viscosity with variation of temperature.

iv) countinuity, rigidity and clarity of films formed.

A starch solution with higher solids content will lead to more amount of starch being present in the final sheet. But for a more uniform distribution of size inside and outside paper surface, a balance has to be struck between the degree of modification and the amount used.

In general, greater the degree of modification, the less the resistance of starch fibre to abrasion or scuffing. Starch used therefore should be modified to the extent, where its viscosity allows adequate amount of starch to be picked up, and still retains a reasonably good scuff resistance. Further the starch should not retrograde, for which it has to be pretreated to reduce the more linear chains. This is generally done by selection of a correct base starch and treating it by oxidation or with enzymes. Suitable modified and formulated grades of starch possessing the necessary characteristics have now become available.

A brief decription of the process of modifying starch with enzymes to make it suitable for paper applications may be interesting. Raw starch if used for enzyme conversion exhibits a wide variance in enzyme suceptibility and results in lack of uniformity of starch solution. Specially buffered starch is now available for enzyme treatment.

Starch	— 20 parts
Water	— 80 parts
alpha enzyme	— required quantity
Heated to 80°C in 7 mt. maintained 80°C for 30 mt.	
Heated to inactivation at 100°C	— 5 mt.
Maintained at 100°C	— 10 mt.
diluted and cooled to 60°C	

Both oxidised starches and enzyme modified starches are preferred to acid converted thin boiling starch. This is due to the fact that in the latter the molecules are not uniformly depolymerised and show retrogradation tendencies.

d) Paper Coating :

Paper coating is still another most important outlet for starch in paper industry. The primary purpose of coating is to enhance the printability and appearance of paper. Casein has been the adhesive used for binding clay and pigments for a number of years, but modified starch in conjunction with synthetic latices is the adhesive currently popular in U.S. and Western countries. This is due to, good adhesive strength, freedom from mildew, low cost and above all ready availability and ease of formulation.

Starch possesses good suspending properties. G.E. Price who has examined various types of starch products for paper coating considers they are comparable with casein. When clay and pigments are worked into paste with equal quantity of water, they form an unworkable dough. Addition of a protective and dispersing agent alters these characteristics so that the mix. acquires flowability. Specially modified starch added to the extent of 15 to 20% on the weight of loading materials gives a coating color possessing good adhesive properties and flowability. Synthetic latices boost binding power further. Addition of ureaformaldehyde precondensate to the extent of 10% on weight of starch improves water resistance. Another advantage starch offers is its resistance to attack by mildew.

e) Paper Converting :

As a reason of its adhesive property starch finds a large market in the conversion of paper to paper boards, boxes, cartons, tubes and many other forms of packaging. This binding power combined with economy make starches formidable competitors to the highly priced synthetics and other adhesives. Before the 2nd World War, technologists of Stein Hall & Co., of U.S. showed how starch adhesive could be used in making corrugated boards. Similarly, in the related field of solid board production, starches are favoured. Starches also find increasing employment for laminating of paper into solid box boards.

f) Speciality Starches :

Vegetable life builds starch granules by combining (polymerising) dextrose molecules. Starch chemists often do the opposite, by breaking up starch polymers into smaller molecules and also by rearrainging or combining them with other radicals. Some of these products are listed below :

i) Thin Boiling Starch (TBS) :

Also known by the name fluidity starches are produced in a range of viscosities and are among the earliest of modified starches manufactured. They are similar to raw starch, except in respect of viscosity of their cooked solutions. They are manufactured by adding acid to a starch suspension and heating to temperature below gelatinsing point. After the degree of conversion has taken place the acid is neutralised and the starch filtered and dried. It is believed that the acid tends to break up the branched amylo-pectin molecules, as a result the amylose fraction becomes more predominant.

ii) Oxidised Starch :

These are noted for their stability and are prepared the same way as the thin boiling starches, except that hypochlorite is used instead of acid. Unlike acid, the hypochlorite acts more uniformly in breaking both amylose and amylo-pectin molecules. It further introduces the solubilising carboxyl group in the molecule to increase stability to jelling.

iii) Cold Water Swelling Starches :

These have the advantage of not requiring cooking and are ready to use. Variations are possible by starting with a modified starch. They are manufactuered by gelatinising starch and drying over heated rolls.

iv) Dextrines :

These are made by heating starch in roasters with or without the addition of acid. They are available in a wide range of viscosities and solubilities. The three main groups are white, yellow and british gum.

v) Other Speciality Starch :

Starch chemistry has explored ways to derive new products from starch by truly chemical means by introduction of new chemical groups and radicals in the starch molecule. These new products have an entirely new structure and exhibit strikingly different properties. The products of commerce are carboxymethyl starch, hydroxyethyl starch and other starch ethers.

From the anionic nature of both cellulose and starch, it would seem that a cationic material would be a natural bridge between fibres. It might be predicted that such a material would have a high degree of retention and exhibit relatively strength increases even when smaller quantities are used, as compared to starch. The cost of cationic starch has been however prohibitive. Dialdehyde starch has been claimed to possess the unique property of improving wet strength of paper.

CONCLUSION :

With the advance in starch technology great progress has been made to develop a large spectrum of products by chemico-physical methods, which offer paper makers a better sheet at minimum cost. Starch is versatile. It finds use as a wet-end additive to improve strength and burst factor. Used as surface size it imparts smoothness, fuzz control and resistance to penetration by oil and printing ink. In paper coating, it binds loading materials to the base paper. As an aid to economical and quality paper making starch products are proving invaluable.

The Indian paper industry has an installed capacity of 7.68 lakhs tons of paper and have a target for making 9.4 lakhs tons by the end of the 4th National Plan. The salient properties of starch, which exhibit potentialities for paper improvement and cost reduction need to be exploited by the Indian paper industry. Here is an area for the starch and the paper technologists to collaborate for their mutual benefit.

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