Cellulose Derivatives-I Scope and Applications

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Cellulose derivatives, which are gaining increasing importance in industry because of their diversified uses, are the cellulose esters and cellulose ethers. These esters and ethers are formed by substituting the hydroxyl groups of cellulose molecule with the respective reagents. The properties and the uses of the products formed depend upon the degree of substitution of the hydroxyl groups and the viscosity of the product. These are the derivatives which are normally handled in the form of liquid and they are water/acid/organic solvents soluble. There is another form of derivatives in which hydrophilic groups are introduced in the cellulose molecule to the extent that it retains its fibrous form and insolubility in water and thus the pulp properties are modified.

The purpose of this paper is to discuss about soluble cellulose derivatives due to their increasing acceptance in industry because of their diversified uses and to reduce dependence on imports. Suitability of the abundantly available raw materials like cotton linters pulp/ dissolving grade wood pulp for the monufacture of different cellulose derivatives is ascertained. Salient features regarding the manufacture of cellulose derivatives like cellulose nitrate, cellulose acetate, CMC methyl/ethyl cellulose are discussed. Technical applications of the above mentioned derivatives are also discussed. Under the scope for future development, it is concluded that, in view of the favourable fibrous raw material situation and because of the possibility of getting process know-how and the equipments needed indigenously, the future of the industry manufacturing cellulose derivatives is very promising. Apart from meeting the domestic requirement a very good export market for cellulose products can also be developed

Introduction

Cellulose derivates are gaining increasing acceptance in industry because of their diversified uses. It is of interest that cellulose derivatives were prepared before cellulose itself was isolated and given a name. At least Bracconnot's preparation of nitrated cotton in 1933[1] was several years earlier than Payen's isolation of the cell wall material which he called cellulose[2]. The preparation of cellulose derivatives became the basis for several industries.

The drivatives which are of greatest interest are cellulose esters and cellulose ethers e g. cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, and cellulose nitrate are esters of cellulose, the respective acids and anhydrides are reacted with the hydroxy groups in the cellulose molecule. Carboxymethyl cellulose, and methyl/ethyl cellulose are ethers of cellulose. These are formed by reacting on alkaline system of cellulose with monochloroacetic acid and methyl/ethyl chloride respectively. In all these reactions substitution of hydroxyl groups could be accomplished to varying degrees by changing the reaction conditions and so also large differences in the properties of cellulose derivative could be obtained. Most of the cellulose derivatives when used are preferably handled in the form of a liquid, they are water/acid/ organic solvents soluble and generally for this sufficiently high substitutions are necessary. Recently interest is shown in other form of derivatives in which hydrophilic groups are introduced in the cellulose molecule to the extent that it retains its fibrous form and insolubility in water. This development is of great significance in paper making where pulp properties are modified to produce paper with superior characteristics which is

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normally not possible with thick stubby films of cotton linters and high yield pulps.

The purpose of this paper is to discuss about soluble cellulose derivatives due to their importance and to reduce dependence on imports. In view of the favourable fibrous raw material situation, there is a possibility of developing an export market for some of these derivatives. For the period from April 1974 to March 1975, the data on the imports (value and quantity) for some important cellulose derivatives is given in Table 1[3]. The value of the imports is of the order of Rupees 34 millions.

Technical Suitability of Available Fibrous Raw Materials for Cellulose Derivatives Production :

For the production of cellulose derivatives purified cotton linters pulp or purified wood pulp is mostly used. Purified wood pulp/dissolving pulp is produced in the country for the manufacture of viscose staple fibre and viscose filament yarn. These purified wood pulps could also be used for the manufacture of ether cellulose derivatives. Source of obtaining purified cellulose is the cotton linters which probably could be made available in significant quantities in the country since India is the third largest cotton producing country in the World. It is reported that presently the demand for cotton linters is limited and if sustained demand is established for the manufacture of cellulose derivatives and many other uses, the availability of linters may reach as high as 100,000 tonnes per year. In view of very high degree purification desired, as measured by the alpha cellulose, minimum inorganic impurities and varying pulp viscosity as determined by Kier boiling and bleaching conditions cotton linter pulp is ideal for manufacture of cellulose acetate, smokeless powder, celluloid etc. Cotton linters pulp lends itself easily for conversion to nitrocellulose. This may be due to smaller number of fibres per gram of unbeaten pulp, the smaller the number of fibres per gram of unbeaten pulp the better does the pulp lend itself to nitration[4]. Nitration grade cotton linters, the easiest fibre to handle has about 2.5 millon fibres per gram, the pulp from Western hemlock and Southern pine about 2.5 to 3 million from red spruce and halsam fir about 6.5 million.

TABLE—I

Imports of Cellulose Derivatives from April 1974 to March 1975

		Quantity (Kg.)	Value (Rs.)
1.	Cellulose acetate flakes.	335,100	1,737,560
2.	Cellulose acetate molding powder.	89,894	400,114
3.	Cellulose Acetobutyrate molding powder.	298,542	3,375,148
4.	Cellulose propionate.	13,525	75,103
5.	Nitro-cellulose.	1,004,550	11,373,567
6.	Ethyl cellulose.	22,181	543,716
7.	Methyl cellulose.	10,834	288,994
8.	Cellulose plastic waste.	1,113,965	4,562,635
9.	Other primary form.	168.028	1,097,345
10.	Cellulose acetate/acetate butyrate (sheet rod, tube)	191,164	2,119,143
11.	Cellulose nitrate/celluloid (sheet tube, rod).	340,625	8,371,228
	Total	3,588,408	33,944,555

General Methods of Preparation of Cellulosic Derivatives : General Considerations :

The degree of esterification or etherification decides the properties of the derivatives formed, and depend upon the following factors :

(1) The condition and composition of the original cellulose. For example its reactivity can

be modified, without chemical change, by swelling (merceri-sation).

(2) The solubility otherwise of the product in the reaction system.

Greater uniformity of the reaction is obtained when the derivative formed is soluble in the reagent mixture as in the case of cellulose acetate. During the nitration of cellulose, where the fibrous structure of cellulose is retained, one has to be very strict about the physical conditions of the cellulose to be nitrated. Cellulose fibres should be uniformly distributed. Execessive moisture results in lower degree of nitration, irregular nitration and temperature rise on dipping. In order to retain its maximum reactivity, cellulose should be dried under vaccum rather than at 105°C as suggested in most of the literature.

Cellulose Nitrate

Following are the main stages (as shown in Figure 1) for the preparation of Nitro–cellulose ;

Nitration :

Out of the different processes for nitration, the most widely used process is the mechanical dipper process.

The composition of the mixed acid to be used is determined by the nature of the cellulosic raw material to be nitrated. Generally the mixed acid is a mixture of sulphuric acid, nitric acid and water in the approximate proportions of 3: 1: 1. A large amount of mixed acid (30 to 50 times the weight of the cellulose) is employed. This high ratio is necessary owing to the bulk of the cellulose and also has the advantage of securing uniformity in nitration, less relative change in the composition of the acid mixture as the reaction proceeds and also the rise of temperature is moderated. The conditions of nitration are decided by the type of the product desired.

Centrifugation :

After the nitration is over the reaction mixture is centrifuged to remove maximum spent acid from the cake of cellulose nitrate. Excessive acid with cake leads to loss of mixed acid, increases pollution problems and washing has to be more rigorous.

Digestion :

After centrifugation the cake of cellulose nitrate is dumped into water for washing, and then boiled with water to remove sulphate ester groups which otherwise tend to make the nitrate unstable. If lacquer grade cellulose nitrate is desired, viscosity of the final product should be low, which can be achieved by number of ways :

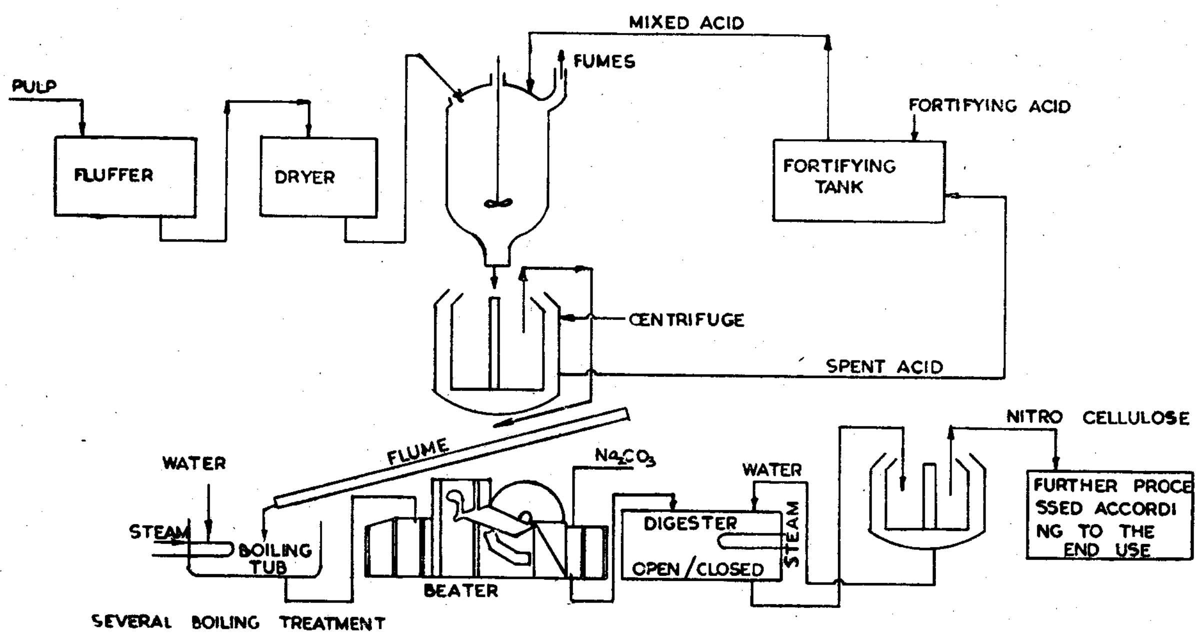

Fig. 1 Flow Sheet for Cellulose Nitrate Manufacture

(1) An increase in the H_2SO_4 : HNO_3 ratio or a reduction in the ratio of mixed acid to cellulose, in increase nitration time/temperature will result in nitrocellulose of lower viscosity.

(2) If cotton linters pulp is used as shown in Figure 2[5], viscosity adjustment can be achieved during Kier-boiling of cotton linters.

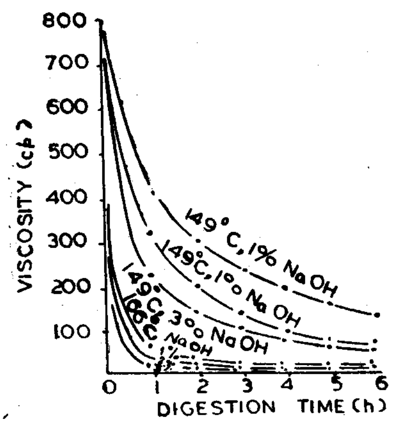

Fig. 2–Effect of Kiering Conditions on Cotton Linters Viscosity

(3) Digestion of cellulose nitrate with water at high temperature (130–150°C), to achieve hydrolytic degradation of the glucosidic bonds, can also reduce the viscosity to the desired value. The rate of viscosity reduction on heating nitro-cellulose under pressure in water at 132°C is shown in Figure 3[6].

For certain industrial uses, such as the manufacture of high grade plastics, nitrocellulose is often bleached (hypochlorite treatment) to remove traces of color, and the bleached nitrate is pressed to

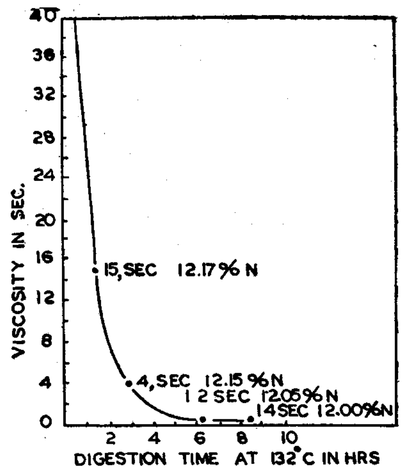

Fig. 3–Rate of Viscosity Reduction of Nitrocellulose on Digestion in Water at 132°C.

blocks, through which ethanol is forced to displace water.

Further Processing of Cellulose Nitrate:

Depending upon its use, the nitro-cellulose is further processed. For lacquers, the nitrate is dissolved in ester solvents, eventually extended with inert diluents such as aromatic hydrocarbons. In case of explosives, the alcohol moist nitrate is gelatinized with ether acetone or nitroglycerin and pressed through a macaroni press. For celluloid plastics, especially films, the usual plasticizer is camphor (around 25 per cent) added along with alcohol and kneaded in a mixer. Afterwards the dough is pressed into blocks, sliced and dried.

Cellulose Acetate (Batch Process):

The process of manufacture of cellulose acetate as shown in Figure 4 involves disintegrating the cellulose to flocks, drying and then pretreating them with acetic acid, esterification to primary or triacetate by acetic anhydride and acetic acid (or any other solvent) in the presence of sulphuric acid or other catalyst at temperature less than 30°C for 5 to 8 hours (till the viscosity drops to the required value). Further hydrolysis to secondary acetate is done on the addition of water to the reaction mixture. Ripening is done at fixed temperature in ripening vessels (shallow copper dishes), time of ripening is according to the required acetyl value. When hydrolysis is reached the desired value, excess mineral acid can be neutralized by addition of sodium acetate. Precipitation of the secondary acetate is done by further water addition. Washing, centrifugation and drying at 20–30°C of the flakes obtained is done Acetic acid is recovered from the spent acid.

Carboxymethyl Cellulose (CMC) (Batch Process):

The first step in the production of CMC is to convert pure cellulose to alkali cellulose by adding caustic soda to cellulose in a a reactor and simultaneously mixing it for one hour. Acid is added slowly for second hour. Mixing is continued for one hour (third hour) after the addition of acid. The temperature of the reaction mixture is controlled between 35 to 40°C by blowing air. Reaction mixture goes to ageing drums for 8 to 10 hours and temperature is between

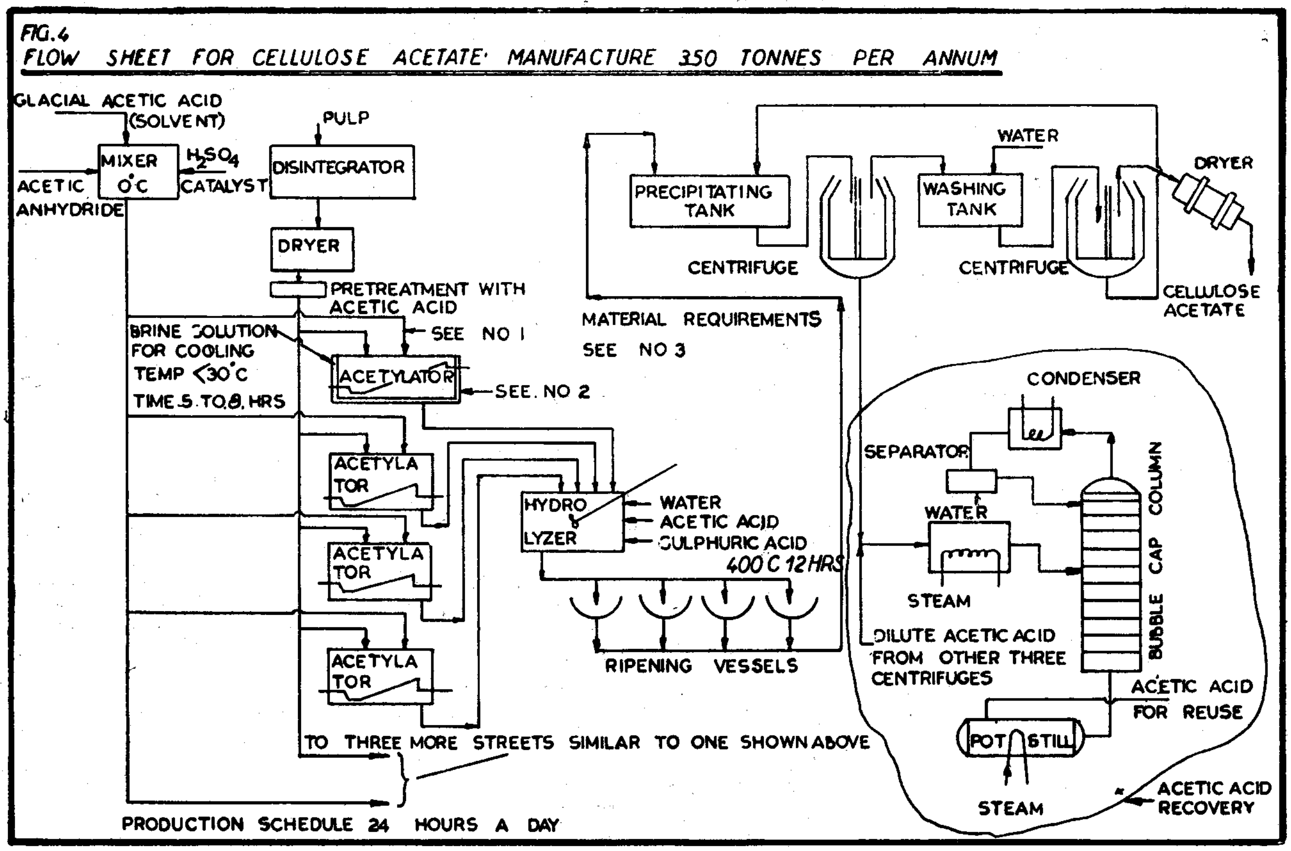

Figure 4

50 to 55°C. After ageing it goes for milling and then for flash drying. Steps mentioned above are shown in figure 5.

Depending upon the end use, CMC is further processed for its purification.

Technical Applications of Cellulose Derivatives:

There are great many uses of the cellulose derivatives, some of which amount to very little from the strictly commercial point of view and a number of these are of great importance. The important cellulose derivatives are briefed, under the specific cellulose derivative, in the following paragraphs:

(1) Cellulose Nitrate:

The nitrogen content of any particular nitrate largely defines its solubility and other properties and consequently its technical application, wnich is as summarized below :

Nitro-cellulose in day to day life is mostly used in lacquers for coating of metals, paper products, textiles, plastics, furnitures, nail polish and playing cards. It is used in large, quantities in flexible packaging materials i.e. cellophane, paper and aluminium foil.

The coating on cellophane is approximately 0.0015 mm thick and add about 10 per cent to the weight of base sheet. For sheets that are to come in contact with water an intermediate coating may be applied between the cellophane sheet and nitro-cellulose coating and thus water vapour transmittance of the uncoated base sheet can be reduced several hundred fold, which results minimum fluctuation in strength and dimensional changes with variations in relative humidity. The coating may also be compounded so that it will heat-seal to itself.

The lacquer coating also improves

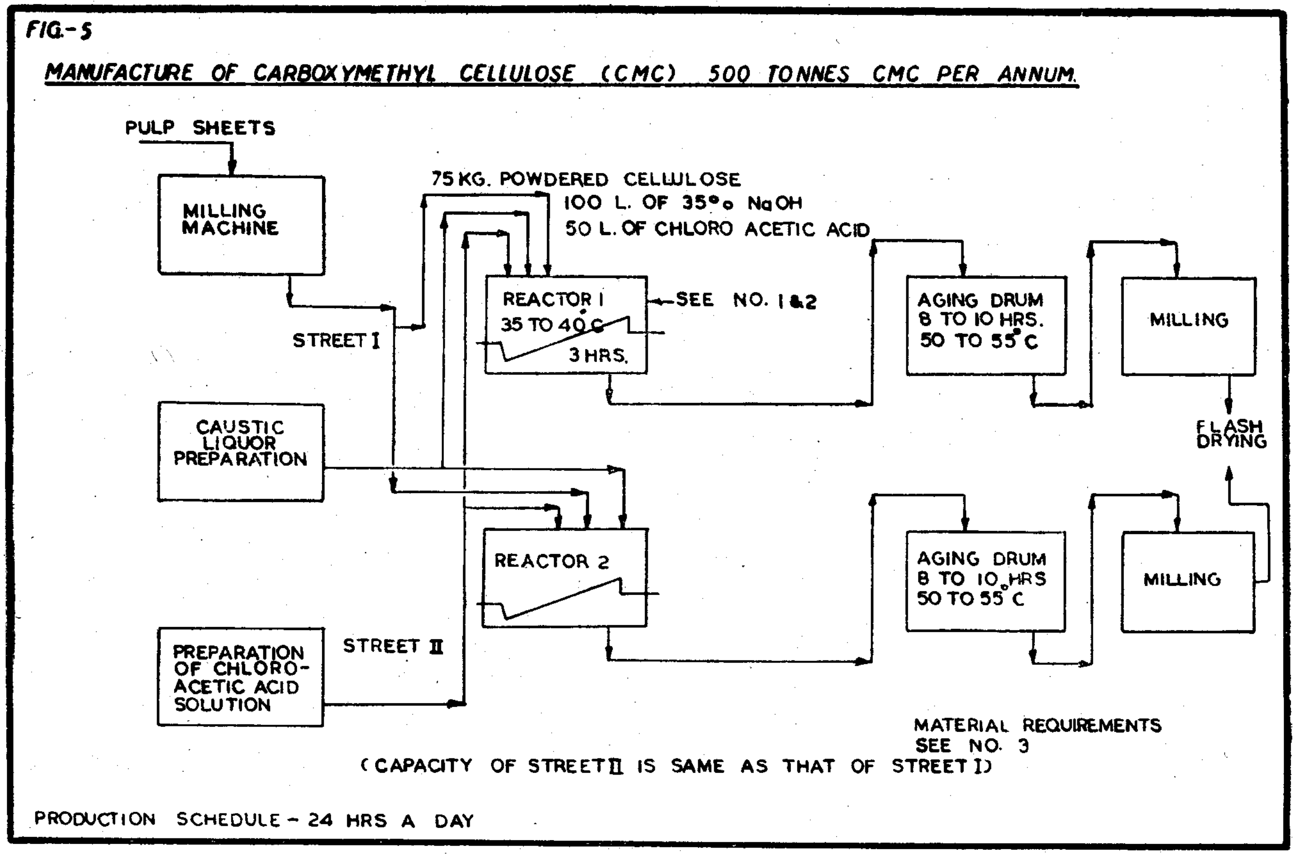

Figure 5.

Nitrogen Content (%)	Field of Application	Common Solvents
10.7—11.2	Celluloid plastics, lacquers. D.P. 500—600	Ethyl alcohol.
11.3—11.7	Photographic films, lacquers.	Ether-alcohol, methyl alcohol, ethyl, butyl and amyl acetate and acetone.
11.8—12.3	Lacquers plastics, gelatinous explosives, cements. D.P. 150-200	—do—
12.4—13.5	For explosives such as smokeless powder. D.P. 2000-3500	Acetone.

the gloss, greaseproofness, gas-proofness and flavour barrier. The coating of playing cards is one of the biggest consumers. Although many other coatings have been tested, none have supplanted nitro-cellulose lacquer as the principal foil coating. The colours or colour combinations are unlimited, as the number of possible lacquer formulations can be prepared.

(2) Cellulose Acetate

Depending upon the degree of acetylation, the grades and uses of cellulose acetates are summarised below :

Sl. No.	Combined acetic acid content (precent)	Grade/used in
1.	52 to 54	Plastics.
2.	54 to 56	Lacquers
3.	55.5 to 56.5	Films.
4.	56.5 to 59.0	Water resisting.
5.	60.5 to 62.5	Triacetate.

Transparency, lack of colour and resistance to heat and light are outsanding characteristics of cellulose acetate in both plastics and lacquers. In plastic field, it is important because of its toughness. It is suitable for both injection moulding and continuous extrusion. Cellulose acetate finds its use in rayon industry also.

(3) Carboxymethyl cellulose (CMC):

CMC is normally used in the following :

Detergents, soaps, food products (specially dietectic foods and ice cream) where it acts as water binder thickener (in water based adhesives such as ureaformaldehyde resins and polyvinyl acetate emulsion). Suspending agent and emulsion stabilizer, textile manufacturing (sizing), coating paper and paper boards to lower porosity, drilling muds, emulsion, paints, protective colloid, pharmaceutical, cosmetics etc.

(4) Ethyl/Methyl Cellulose:

Ethyl/Methyl cellulose is a cellulose ether in which ethyl/methyl groups have replaced the hydrogen of the hydroxyl group. The alkali cellulose is alkylated with reagents such as ethyl/methyl chloride or ethyl/methyl sulphate. Ethyl cellulose plastics may be molded in any manner or machined. Some of the outstanding properties are unusually good e.g. low temperature flexibility and toughness, wide range of compatibility, stability to heat thermoplasticity, and electrical resistance.[1]

Methyl cellulose has got the advantage of water solubility, plus the ability to produce viscous solutions which had made it useful for a thickening agent in the textile, food and adhesive industries.

Scope For Future Development :

India being the third largest country in the world for cotton production and will continue to be so, for long time to come, thus any industry based on cotton will always have a good growth potential. The potential availability of cotton linters in the country is such that it can produce 70,000 tonnes per year of superior quality pulp. Presently, dissolving grade wood pulp is also prepared indigenously. There is possibility of getting the process know-how and the equipments needed (for batch processes) indigenously.

Cellulose derivatives, if produced in the country from the most abundantly available cotton linters pulp, can save large foreign exchange outflow which is now being spent on importing different type of cellulose derivatives (worth around Rs 34 millions), as shown in Table I.

Advance in the field of cellulose derivatives can lead to the development of other chemical industries in the country.

The superiority of cotton linters pulp over wood pulp for the production of cellulose derivatives suggests that India can not only achieve the import substitution, but can comfortably compete with Scandinavian countries (mostly using coniferous woods) for the export of cellulose derivatives.

Thus in view of the above factors the future of the cellulose derivatives industry in India is very promising.

References:

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5. Rydholm, S.A., Pulping Processes, p 1017 Interscience Publishers (1965).
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Discussion:

Mr. P.S. Hariharkrishanan (Travancore Rayons)—What are types of cellulose derivative imported in India ?

Dr. S.C. Kansal—The imports from April 1974, to March 1975 consist of cellulose acetate (flakes and molding powder), cellulose acetobutyrate (molding powder), cellulose propionate, nitrocellulose, ethyl/methyl cellulose, cellulose nitrate (celluloid in the form of sheet, tube and rod).

Mr. H.R. Mohan (S.P.B. Ltd.)—Could you give us some more details regarding present state of research (with reference to cellulose derivatives) in India ?

Dr. S.C. Kansal—G. Shankar and J.S. Chawla have worked on waste cellulosic raw materials for producing cellulose derivatives (Na CMC). Their work is published in IPPTA issues of 1972 and 1973.

Mr. H.R. Mohan--Could you give us some idea about the concerns in India which are engaged in meeting the demand of equipments required for manufacture of cellulose derivatives ?

Dr. S.C. Kansal--Presently there is no machinery manufacturer who can supply full plant for cellulose derivatives manufacture as in the case for small capacity paper manufacture number of machinery manufacturers in India can supply full plant for the said purpose. From the developments which we have achieved in the field of oellulose derivatives, we are sure that individual equipments needed can be designed and fabricated as per the requirements.

Mr. Jacob Samuel (Gwalior Rayons)—What are the types of CMC that can be prepared from wood pulp ? Is it possible to make high viscosity CMC from wood pulp ? Why many of the manufacturers of CMC prefer cotton linter pulp ?

Dr. S.C. Kansal—Depending of the purity and reactive groups and on the degree of polymerisation (D.P.) of the bleached pulp almost all types of CMC can be prepared from wood pulp. But for high viscosity CMC cotton linter pulp is preferred because cotton linters give purified cellulose and products of varying viscosity can be prepared from cotton linter pulp whereas this is not there in case of dissolving grade wood pulp.