Some Aspects in the Manufacture and Use of Dissolving Pulps

By

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DISSOLVING Grade pulps bear deep contrast to the pulps used for paper making. In the manufacture of paper, the primary requirement is of fibre with certain physical qualities and chemical composition is less important except as it affects the physical behaviour of the fibre. For pulps going to make another large class of cellulosic products, the relative emphasis on the above two factors is reversed. These products are made by chemical reaction processes in which cellulose is usually taken into solution. In this case chemical structure and composition of the pulp form the primary concern and the physical form of the pulp is significant only in the first stages of the process. Based on the fact that cellulose goes into solution, such pulps are termed "Dissolving Pulps" or Chemical Cellulose.

It will be interesting to note that the term "Dissolving Pulp" covers a more extensive range than "Rayon Grade" Pulp. Rayon Pulp is suitable for all Rayon Fibres and Cellophane whereas the Pulp suitable for Rayon is unsuitable in the manufacture of Tyre Cord Yarn and polynosics, which, although made by the same viscose process, require pulp of the highest purity.

A wide variety of products is manufactured from such Dissolving Pulps.

(i) Textile and Industrial Yarns and Fibres. Mainly filament Rayon, Staple Fibre, Tyre Cord, H.W.M. (High Wet Modulus) Polynosic Fibres, all by Viscose process.

Diacetate Yarn & Fortisan (High strength Acetate Yarn)

(ii) Films & sheets mainly Cellophane or Cellulose Film, Cellulose Triacetates for photographic films, Cellulose moulding powders, filters etc.

(iii) Plastics and moulded articles like collodion, celluloid, acetate moulded materials, etc.

(iv) Special chemicals e.g. cellulose nitrates for ammonition and for lacquers, carboxy methyl cellulose and other esthers.

For all the above end uses, the basic requirements are high quality and purity of the pulp. The main quality requirements for dissolving grade pulps in different lines of Rayon/Cellophane manufacture and the impact of each of these characteristics on Viscose processing are attempted to be discussed.

I. High Alpha Cellulose

The α cellulose content of dissolving pulp is of vital importance, a minimum of 90% requiring to be ensured for proper Viscose processing. This is because the Rayon yield depends directly on the α cellulose in the pulp, so much so that the estimation of Rayon yield has almost come to replace α estimation. The stipulations of α cellulose in pulp differ from one end use to the other. For acetylation and nitration, a minimum of 99% is specified. (Please refer specification table in Annexure).

Hemicelluloses

The α cellulose content is vitiated by hemicelluloses, which form the principal non-cellulosic polysacharides present in the pulp. They are low molecular weight substances, degraded by acid prehydrolysis more rapidly than cellulose and extractable with alkaline solution much more than cellulose. The average D.P. of hemicellulose may be less than 200. The presence of hemicellulose in Viscose Pulp will affect the process by

(a) Causing deterioration of the mechanical properties, e.g. wet strength of the fibre.

(b) Interfering with the reaction velocity of xanthation, by getting xanthated faster than cellulose, consuming excess of CS_2 and thereby vitiating the uniformity of xanthation and causing deterioration of Viscose properties.

(c) Hindering the process of ageing or maturing of alkali cellulose. The hemicelluloses contain more aldehyde groups than cellulose and consume more oxygen for their oxidation.

Lignin

The presence of residual lignin in the pulp adversely affects the Viscose process by

(a) Reducing the reactivity of cellulose including its swelling and solubility properties.

(b) Reducing the solubility of xanthate resulting in poor filterability of Viscose.

(c) Inhibiting the ageing of alkali cellulose. This is shown by the much faster ageing of alkali cellulose from Cotton Linters (without lignin) than from wood pulp.

(d) Rendering the fibre hard.

For estimating lignin, apart from the indirect methods of Permanganate No., Kappa No. etc. a new method using Cadoxen (Cadmium Ethylene) as a solvent is a new development.

II. **Low Ash and Mineral Matter**

The ash content in dissolving pulps can be classified into two groups:

(1) **Metal Salts :** e.g. Mn, Co, Ni & Cr. These metal salts act as catalysts and increase the oxidation of cellulose in the alkaline medium. Iron, Co & Mn have specific effects on the maturing of alkali cellulose and disturb the Viscose process.

Some other metal salts e.g. Pb, Be, Al, Cu etc. behave differently and inhibit the oxidation of alkali cellulose. The presence of Mn and Cu salts is also known to cause cellulose degradation to form oxycelluloses.

The maximum permissible limit for Mn in dissolving pulps is .2 ppm and for Cu 3 ppm. For tyre cord and polynosics, these limits are .1 ppm and 1 ppm for Mn and Cu respectively.

(2) **Silica**: The epidermal cells of plants are very rich in silica and hence the occurrence of silica in dissolving pulps manufactured from all fibrous raw materials. A high silica content can affect the Viscose process by rendering the viscose solution turbid, by slowing down the filtration process and also by affecting the strength properties of the final product. Great Care has to be exercised by the Pulp Maker to eliminate silica in the cooking and bleaching operations and also by employing suitable riffling devices, centricleaners etc.

III. **Brightness :** of the pulp should be high as the colour of the final product depends much on the initial brightness of the pulp. Good brightness and colour are to be obtained in the bleaching and finishing stages, taking due care to control depolymerisation. The use of elemental chlorine, chlorine dioxide etc. will help in achieving high brightness. The use of optical brighteners is not advisable for reasons of both cost and adverse side effects.

IV. **Uniform D.P. Distribution and Strength Properties :**

The D.P. is an important parameter indicating the strength characteristics of the pulp and also of the final product. The D.P. which bears upon the molecular weight is assessed in terms of viscosity of a solution of the pulp and computed by means of a D.P. Chart. The Viscosity is alternatively obtained in terms of the reciprocal measure of its fluidity. Determination of fluidity, being easier, is getting to be more accepted recently. The viscosity/fluidity is a vital characteristic for the Pulp Maker as well as the Pulp Consumer. For the former, the viscosity reveals the extent to which rendering or degradation of the cellulose has occurred during the cooking and bleaching operations and aids in controlling his process. In the case of the latter, viscosity is the important basis for control of the ageing/maturing process in such a way that best spinning conditions as well as good strength properties for the final product are ensured.

In a process employing more than one type of pulp in a blend, it is necessary that the D.Ps. are synchronised to be more or less at the same level so as to get uniform conditions in viscose as well as in the final regenerated cellulose. It sometimes happens that due to reasons of availability or cost, 2-3 differnt pulps have to be blended and such situations pose a challenge to the Processman.

Among the various dissolving

pulps, it is seen that cotton linter pulp and Prehydrolysis Sulphate Pulp give a narrower D.P. Distribution than sulphite pulps.

V. Reactivity and Filterability :

The reactivity of dissolving pulp refers to its behaviour and smooth performance in Viscose processing. Different pulps behave differently in the steeping stage, ageing and xanthation. The cumulative effect of various impurities in the pulp bears upon xanthation and filterability. The state of the Viscose solution with reference to particle size, gel distribution and ripening is also important. The ultimate yarn/film spinnability and properties like tensile strength and elongation depend on the Viscose which in turn depend on the pulp from which it is made. The most important Viscose tests are filterability estimations, gel particle count and in the case of tyre cord pulp, estimation of particle size distribution by sophisticated instruments known as Scanning Electron Microscope (SEM).

The features of reactivity and filterability of dissolving pulp are intertwined to each other such that one cannot draw a clear line between these. Deficiencies in reactivity usually tell upon filterability and spinnability.

The reactivity of pulp depends on a number of factors ranging from the species and cleanliness of the wood or cotton linters used, the process of pulping and bleaching adopted, the quality of water used, the chain length distribution of cellulose molecules, the crystalline or amorphous nature and its distribution and alignment in the fibres and the nature and extent of organic and inorganic impurities present. In all wood species, the Parenchyma cells form a constituent. These cells contain high alcohol-benzene extractives, high lignin, high ash and less cellulose. The pulp reactivity would depend on how efficiently these cells are eliminated in Pulp making. The lingering presence of Parenchyma cells in the finished dissolving pulp is reported to lead to ball formation during xanthation, to resist alkali penetration and to render Viscose hazy. The presence of pentosans in the pulp also may affect the reactivity, although the major portion of them may get removed in alkalisation. High pentosan content in pulp causes uneven xanthation, the presence of unreacted fibres, gel particles and reduced filterability.

Particle size distribution of impurities like rust, lime and sand also affects filtration. Sub-microscopic particles of size below 20 microns pass through the filter media but block the spinnerets. Particles of size between 20-100 microns cause filter clogging. A high calcium content in the pulp precipitates hemicellulose in the recycled soda lye and also damages the spinnerettes by forming incrustrations.

The reactivity of dissolving pulp is measured and expressed in terms of clogging constant Kw 20, 40 where the 20, 40 denote the weight of viscose collected in 20 and 40 minutes. Standard estimations are expressed in terms of filter ratio and filter constant etc.

It is reported that Hot Alkali Extraction, after bleaching of the pulp helps in increased reactivity and filterability of the pulp by transforming the fibre into transverse discs whereby uniform and complete esterification is brought about and also by eliminating oxycellulose groups possibly formed during the bleaching.

The use of the ClO_2 in the final bleaching stage and sulphurous acid in the last stage are side to impart better reactivity to the pulp.

(vi) Resin Content :

The resin content of dissolving pulps should not be high as it will affect the colour of the Rayon or Transparency of the film. If it is higher than .2%, the end product also becomes yellow and processing difficulties are encountered but at the same time, the presence of a small amount of resin in the pulp is desirable and helpful. If resin is less than .15%, process and filtration difficulties arise. This is because resin serves as a contact angle regulator between CS_2 and alkali cellulose. To overcome such situation which are common when prehydrolysis sulphate pulp or cotton linter pulp are used, some surfactants require to be added.

Integration of Dissolving Pulp and Viscose Units

When the manufacturing of the dissolving pulp and of Viscose fibre/film are separate units away from one another, they are considered as different units, the Pulp Maker becoming a seller and the Viscose Maker, a buyer. For want of perfect appraisal and understanding of each other's problems, the interest of both the units are often allowed to suffer. The orientation of both units to an integrated pulp and fibre unit will be the panacea for such problems.

New Analytical Tests For Dissolving Pulps

Some additional analytical tests are needed to control dissolving pulp quaility in the pulp mill. If, in addition to the congentional pulp analysis some additional criteria correlating the pulp characteristics to the Viscose processing are also introduced, this will go a long way in resolving the problems of both the pulp and fibre units to mutual advantages. Examples of such criteria will be

		∝ Cellulose
Commercial value of pulp in terms of cellulose and Viscose yield	...	R—18
Effects of the pulp on Viscose production	...	R—18 Moisture, Viscosity, Ash, Ether Extract.
Effects of the pulp on Viscose spinning	...	Ether Extract, Hemi Lignin, Iron, Reactivity, Filterability
Effects of the pulp on final product	...	D.P. Distribution Brightness, Reactivity.

It is in this background that the modern trend is towards an in'egrated pulp and fibre unit, rather than to having the pulp and fibres as separate units.

The sum up, the progress made in respect of Dissolving Pulp production in our country has been remarkable. Without allowing any complacency to set in, we have to advance further in this technology and catch up with the foreign countries. All India Technical Bodies like IPPTA could formulate measures for intensive technical training opportunities and exchange of know-how in this field, so that all round growth is possible on a national scale.

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The author gratefully acknowledges reference to the following literature on Dissolving Pulps.

(1) Hand-book of Pulp & Paper Technology by Kenneth Britt.

(2) Hand-book of Rayon (Century Rayons).

(3) TAPPI Dissolving Pulp, Conference—Oct. '73.

Specifications for nitration (Cotton Linter Pulp)

Characteristic	*For Explosives grade Nitrocellulose*	*For Lacquer grade Nitrocellulose*
Moisture	7.0	7.0
Acidity to Cargo Red	Nil	Nil
Mineral Matter %	0.25	0.15
Ether Solubles%	0.25	0.25
Solubility in 3% NaOH%	3.00	3.00
Cellulose % Min.	99.0	99.00
Malachite green dye test	Must pass	Must pass
Copper No.	1.00	1.00
Viscosity in poises 2% sodium	5-50	5-50
Fibre length	—	—
Brightness (Flrepho) min.	85	90

INDIAN STANDARDS I.S. 1966

Requirements of chemical cotton (Cotton Linters)

Sl. No.	*Characteristics*	*Requirements for* *Type 1	*Type 2*	*Type 3*	*Type 4*	*Methods of test-I.S. 3518-1966*
I	Moisture per cent max.	7.5	7.5	7.5	7.5	3
II	Alpha cellulose Min	98.0	98.5	99.0	99.0	4
III	Solubility in 7.14 per cent sodium hydroxide max.	2.0	2.0	2.0	2.0	5
IV	Solubility in 1 per cent sodium hydroxide max.	—	1.4	—	—	6
V	Ether soluble matter per cent max.	0.1	0.05	0.1	0.1	7
VI	Ash content per cent max.	0.1	0.1	0.1	0.1	9
VII	Acid insoluble ash ppm max.	75	50	80	80	10
VIII	Iron as Fe, ppm max.	50	10	40	40	11
IX	Manganese as Mn. ppm max.	0.2	0.2	—	—	12
X	Calcium as Cao ppm max.	120	50	50	50	13
XI	Pentosand content, per cent max.	0.3	0.3	0.3	0.3	14
XII	Brightness per cent min.	85	85	85	85	15
XIII	Fluidity (Rhes) 0.5 g in 100 ml. solution	16.5 to 18	16.5 to 18	5.0 to 11	5.0 to 7.5	16

Type 1 for use in Viscose rayon and film.
Type 2 for use in high tenacity viscose rayon.
Type 3 for use in cellulose acetate yarn.
Type 4 for use in cellulose acetate plastics.

Typical Specification for Dissolving Pulp

	Buckye
Cellulose	98.5
Beta	1.3
Gamma	0.4
Viscosity 5% CED	8.5
D.P.	1354
S.S.	2.0
S. 10	1.7
S. 18	0.7
S. 21.5	0.5
Ash %	0.5
Silica ppm	32
Calcium	35
Mn.	8
Iron	0.4
Alcohol Benz. Extract	0.04

Specifications of dissolving pulps of 3 different grades filament rayon, tyre cord yarn and polynosic fibres

Properties	*Dissolving pulp for Rayon Continuous filaments*	*Dissolving pulp for tyre cord yarn*	*Dissolving pulp for Polynosic fibres*
Alpha cellulose %	93 - 93.5	97 - 97.5	95 - 96
Beta Cellulose %	2.2 - 4.0	1.9 - 2.8	3
Gamma Cellulose %	2 - 4	1 - 2.6	2 - 3
Pentosans %	3.5 - 4.5	1.0 - 2.7	2.7 - 4.0
Ash %	0.05 - 0.10	0.05	0.05 - 0.07
SiO_2 ppm	15 - 40	15 - 23	15 - 25
Ca+Mg ppm	70 - 180	10 - 20	10 - 20
Fe ppm	3 - 4	2	2
Cu ppm	2 - 4	1	1
Mn ppm	0.1 - 0.2	0.1	0.1
Resin (alcohol benzene solubility) %	0.15 - 0.20	0.15	0.15 - 0.20
Copper Number	1.0 - 1.2	0.8	0.7 - 0.8
Degree of polymerisation	850 - 1000	1000 - 1000	1100 - 1200
Brightness GE	93 - 94	90 - 93	91 - 93
Moisture content %	6 - 7	6 - 7	6 - 7
Sheet substance g/m^2	650 - 750	650 - 750	650 - 750
Sheet thickness mm	0.85 - 1.2	0.90	0.9 - 1.0
Sheet apparent density g/cc	0.65 - 0.75	0.65 - 0.75	0.65 - 0.75