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MANUFACTURE OF DISSOLVING PULP FROM EXOTIC RAW MATERIALS 1/

by

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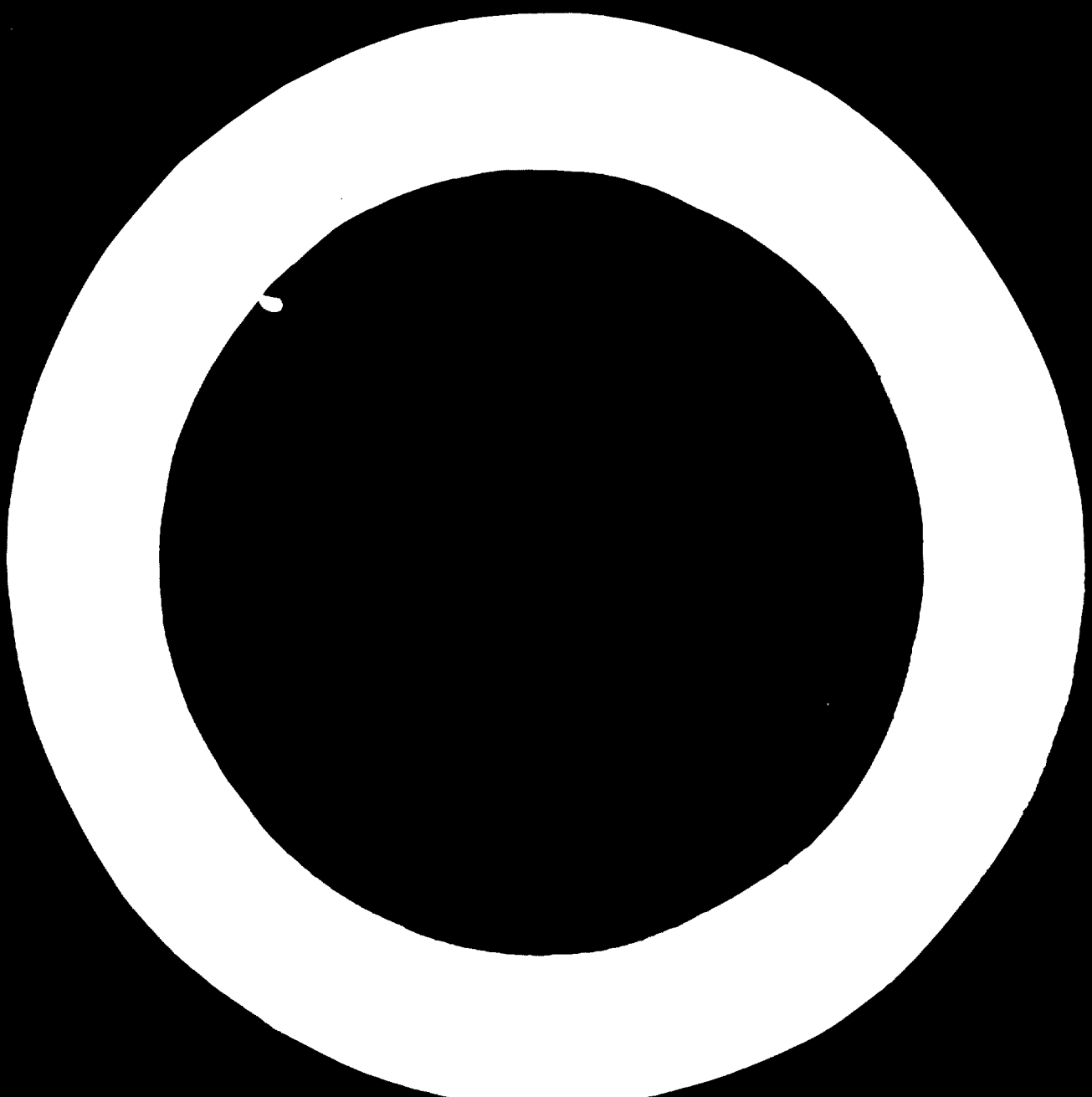

I. INTRODUCTION :

In contrast to paper pulps , dissolving pulps are subjected to several chemical treatments with the object of converting them to different cellulose derivatives. These derivatives , unlike cellulose itself , are soluble in dilute alkalies , cheap organic solvents or even water. In several industries , cellulose and cellulose derivatives are regenerated from solutions in the form of fibers , films , or sheetings. Solutions of cellulose esters and ethers are the bases for several lacquer formulas and surface coatings. One of cellulose derivatives namely nitrocellulose (cellulose nitrate) is used as well, in explosive industries. The water-soluble sodium salt of carboxymethyl cellulose is used as a sizing agent in textile industry (as a substitute for starch) , as adhesive in paper making or as thickening agent in food and cosmetic industries. The first known plastics were manufactured from cellulose derivatives.

In the early stages of cellulose industries i.e. in the last decade of the 19th. Century , purified cotton linters were the main source of cellulose products. High alpha-cellulose

pulps i.e. dissolving pulps produced from wood have then steadily replaced linters especially in viscose rayon industry. Softwoods were the first raw materials used for production of dissolving pulps. Later on , hardwoods found their way to dissolving pulp industry. From non-wood raw materials , only reeds have been used for some times in a few countries as Italy and Romania.(1.) Nevertheless , reed pulp constituted a negligible fraction of dissolving pulp production. It was reported that wheat straw had been used in Germeny on an industrial scale for dissolving pulp manufacture during world war II(1.). A tremendous number of research articles , reports , and studies on exotic raw materials as sources for dissolving pulps have been published in the last 30 years. Just to give the references of these articles would fill a great number of pages. In this paper only a review of the most important articles relating to the basic features of the subject would be refered to as far as possible. Most of the studies on exotic raw materials ceased at the point where pulps of high alpha-cellulose content were obtained and analysed. Continuation of the studies to preparation of cellulose derivatives till the end product in a manner which simulates the industrial processing is usually not undertaken because of the relatively high costs and efforts. Chemical and physical analytical data are not sufficient for evaluating dissolving pulps. Such data give only a preliminary idea but cannot predict the behaviour of the pulp during the many operations to which it is subjected till the end product say viscose rayon filaments are produced. Several standard tests have been

proposed for evaluation of dissolving pulps , but these are not always correlated to pulp behaviour during the different manufacturing operations. The last word for pulp evaluation is still the result obtained from the simulation of all industrial preparation and treatment operations. Small scale pilot units have proved to be more or less satisfactory.

To start discussing the suitability of exotic raw materials for the manufacture of dissolving pulps it is felt necessary to give at first a brief account of the different grades of dissolving pulps. As before mentioned , dissolving pulps are used for manufacture of a great variety of cellulose products ranging from cosmetics to explosives. Therefore it is natural that there are different specifications for dissolving pulps according to the purpose for which they are used.

II. GRADES OF DISSOLVING PULPS :

1. Viscose grade pulp:

Pulps to be used for viscose rayon manufacture should possess relatively high alpha-cellulose content. The presence, however of a considerable percentage of Hemicelluloses is permissible. These are removed to a great extent during mercerization and pressing of the pulp while preparing alkali cellulose in the viscose factory itself. Table 1 represents general chemical and physical analytical data which are requested in viscose pulps ([2]). Alpha-cellulose could be as low as 88% in these pulps. As regards ash , some of its constituents are

Silica is almost the main negative factor. The presence of more than 0.05 % silica in pulp leads to clogging of the filter cloth while filtering viscose (3). Especially pulps obtained from non-wood raw materials are characterized by high ash content and in several cases silica makes up more than 50 % of the ash.

2. Acetate grade pulp :

Pulps to be used for cellulose acetate manufacture should possess higher alpha-cellulose than viscose pulps. The alpha-cellulose content is usually higher than 97 % . Non cellulosic components such as Hemicelluloses , ash , and silica should be much lesser than for specifications of viscose pulps (4). Cellulose acetate is used for production of rayon as well as films , lacquers , and plastics. The non-cellulosic impurities cause insoluble residues leading to haze which are objectionable especially in films and lacquers. Viscosity of acetate pulps should be lower than that for viscose pulps, but this can be easily adjusted during pulp manufacture.

3. Nitrate grade pulp :

Generally speaking nitrate pulps should possess as high alpha-cellulose as acetate pulps. However higher ash and silica contents are permissible as far as the prepared cellulose nitrate is not used for films and lacquers.

4. Ether grade pulp :

This pulp grade should be of more or less the same purity as acetate pulps. However for the specific case of the sodium salt of carboxymethyl cellulose (Na CMC) much lower pulp purity

is tolerated. This water-soluble ether (Na CMC) is not used in films , lacquers , or plastics. It is used in the form of aqueous solutions for drilling purposes even without eliminating the byproducts formed during the preparation of this derivative from the pulp. For the use of Na CMC as a sizing agent in textile industry or as adhesive in paper making , the presence of inorganic residues or Hemicelluloses would apparently cause no difficulties.

Summing up , viscose grade pulps and carboxymethyl grade pulps do not require high purity as those necessary for acetate or nitrate pulps. Nitrate pulps for explosives industry could contain somewhat higher inorganic residues than acetate pulps.

III. PREREQUISITE OF DISSOLVING PULP AS A CELLULOSE REACTANT:

Pulp consists of different cell types which may vary much in their chemical composition. Accordingly , the analytical chemical data given in Table 1 for a viscose pulp represent only an overall average. It thus becomes evident that a pulp does not represent a pure cellulose reactant with constant chemical data but rather a heterogeneous mixture of reactants. What makes the picture more complicated is the fact that also the fine or microstructure of different cell types show much differences. By fiber fine structure is generally meant " the microstructure of the cell wall " or in other words the degree of packing or adhesion of the elementary fibrils within the cell wall as well as the degree of packing of cellulose molecules within the elementary fibrils.

Table 1 : Chemical requirements of a suitable rayon grade pulp.

Alpha cellulose,	%	Greater than 88.0
Soluble in alcohol benzene	%	Less than 0.5
Pentosan,	%	Less than 5.0
Ash,	%	Less than 0.15
Lignin,	%	Less than 0.10
Brightness,	%	Greater than 85.0
Viscosity (Tappi),	CP	1 to 25

The fine structure of pulp fibers depends upon the raw material , the pulping process used , purifications conditions , and drying conditions. Fiber fine structure affects the diffusion resistance of the cell wall to chemical reagents i.e. affects swellability or rate and extent of exposure of cellulose surfaces and hence reactivity. Most cellulose industrial reactions belong to the the heterogeneous type at least in the early reaction stage where cellulose is still retaining its fibrous structure. As in all heterogeneous reactions the reagent molecules have at first to diffuse into the micro voids and capillaries of the fiber till they can reach cellulose surfaces. Thus the innermost surfaces will react at last. The diffusion rate in most of such reactions is lower than the rate of the chemical reaction proper (5). Therefore it is the diffusion rate which governs the overall reaction rate. Since different pulps and different cell types in a pulp possess different fine structure therefore they possess different diffusion resistance to reagents. Respectively the different pulps and different cell types in each pulp react at different rates , and after a certain time period they show different degrees of substitution (D.S.) of the cellulose functional hydroxyl groups. For instance , upon xanthation of alkali cellulose with CS_2, less than 1/3 of the hydroxyl groups of cellulose are sufficient to be substituted to obtain solubility in dilute alkali to give viscose (6). If the pulp is too heterogeneous , the most reactive cell types will consume more CS_2 (i.e. will be over-xanthated) and hence the least reactive

fibers will be insufficiently xanthated and do not go properly in solution.

Softwood pulps are composed of almost one type of cells namely trachieds of similar chemical composition and similar microstructure. Therefore high alpha-cellulose softwood pulp represent one of the most homogeneoue celluloses. Accordingly , softwood pulps are - beside purified cotton linters - the best suitable for industrial diesolving pulps. Hardwoods possess a more heterogeneoue anatomical structure than softwoods. In other words hardwood pulps contain more different typee of cells. As before mentioned this pulp heterogenity could lead to some difficulties during the manufacture of cellulose derivatives. Non-wood raw materials are still more heterogeneous in anatomical nature and generally speaking these materials would be of less suitability for dissolving purposes than wood.

In the foregoing it was explained why the pulp analytical chemical and physical data alone are far from being sufficient for evaluating pulp suitability for different cellulose industries. This fact led a tremendous number of research workers to look for standard tests depending upon reactivity measurement of the pulp towards specific reactions. Such methods imply measuring the reaction rate by determining the D.S. and /or solubility till equilibrium is reached(e.g. 7). Reactivity measurements

although represent a step further - than just pulp chemical analysis - towards pulp evaluation yet they still do not stand in a clear-cut relationship with what really happens during the industrial working up of the pulp. Therefor the final and conclusive evaluation of a pulp respectively a raw material for a certain cellulose industry is delivered by simulating all manufacturing operations on a small scale in the laboratory and testing each operation and each cellulose intermediate till the end product itself is obtained.

Such methods are described in brief in the following.

IV. EVALUATION TESTS OF DISSOLVING PULPS BY PARTIAL OR TOTAL CONVERSION TILL THE END PRODUCT UNDER SIMULATION OF MANUFACTURING OPERATIONS :

1. Tests for viscose grade pulps :

In viscose rayon or cellophane manufacture , pulp in the form of sheets is soaked in 17.5 % NaOH solution. The soaked pulp is pressed to a certain press ratio to eliminate the excess sodium hydroxide solution. In another method the pulp is treated in a slurry form. The formed alkali cellulose is shredded , aged , then xanthated. The xanthate is then dissolved in dilute sodium hydroxide solution to deliver viscose. The produced viscose can be tested for several properties as content of gel particles , turbidity , ..etc. However the most important technical property of viscose is its filterability. During manufacture , viscose is filtered in filter

presses and it is necessary that the filter cloth does not get clogged quickly. In this respect a standard method for determining the decrease in filteration rate has been developed. By measuring the rate of filteration over a relatively short time period , a constant termed filter clogging constant or (Kw) can be found out (8). The smaller the magnitude of Kw , the better is the filterability. In the present paper , the reported data of Kw are the results of experiments carried out in a small viscose pilot plant (9). The used batch is about 100 grams pulp (B.D.). The viscose after filteration and ripening can be spun into continuous filaments which are then to be tested and compared with commercial rayon.

2. Tests for acetate grade pulps :

In acetate rayon manufacture , the pulp is at first steeped in glacial acetic acid which has more swelling effect on fibers than the acetylating mixture itself. To the pretreated pulp an excess of glacial acetic acid and acetic anhydride is added into a closed vessel fitted with a stirrer in the presence of sulphuric acid as catalyst. The reaction mixture is left for several hours at 25-30 °C. The mass becomes gelatinous and the pulp dissolves almost completely and at the end of the reaction , cellulose is converted to the triacetate. The triacetate is then transformed into the acetone-soluble diacetate through hydrolysis by adding water to the mixture. The whole mixture is then poured into excess of water where the acetate precipitates into the form of chalky flakes. These are ground,

dissolved in acetone and spun to rayon.

Sevearl tests can be carried out to check each of these preparation steps. one test depends upon determining the residue and turbidity of the acetylating mixture at the point when the pulp has been completely converted to the triacetate. In the present paper the results given are according to the method of Jayme and Schenck (10). The turbidity was estimated also after centrifuging the solution by a Hilger-Speker Absorptiometer and flourimeter with pair of neutral filter for turbidity measurements. It is more informative to go a step further and prepare the diacetate and test it. For diacetate preparation , the method of Sieber (11) was used in the experiments reported in this present paper. The precipitated diacetate was stabilized by boiling with water containing 0.015 % sulfuric acid for 5 minutes then ball milled after being dried. According to standard specifications (12) , the diacetate should possess ash content lower than 0.2 %. Acidity calculated as free acetic acid should not exceed 0.01 % by weight. Stability as liberated acetic acid should not exceed 0.5 % by weight. Charring point should not be lower than 200°C. (however , the higher the better) and solubility in acetone not lower than 99.9 %.

3. Tests for nitrate grade pulps :

For the manufacture of cellulose nitrate , the pulp is treated with nitric-sulfuric acid mixtures of different compositions

depending upon the required nitrogen content in the nitrate. The nitrate is then stabilized and tested for different properties. The most important property , however , is the stability and solubility in ether-alcohol mixtures. As far as the nitrate is not intended to be used for films or lacquers , the stability test would be sufficient.

4. Tests for ether grade pulps :

The tests given here are for specific ether derivative namely the sodium salt of CMC. There are several methods for manufacturing this derivative. In one method the pulp is treated with sodium hydroxide solution of higher concentration than that used for mercerization in the viscose process. After removing the the excess alkali , the formed alkali cellulose is shredded with monochloroacetic acid or sodium chloroacetate and the reaction is carried out to the desired D.S. Usually a D.S. of at least 0.4 is necessary to obtain a water-soluble product. Beside the formation of NaCMC , sodium chloride and sodium glycolate are formed as byproducts. The whole reaction mass can directly be applied without purification in the case of drilling operations. However , for other purposes the reaction products are dissolved in dilute sodium hydroxide solution then filtered. The filtered solution is neutralized with CO_2 to exhaust the free alkali. The filterability of the solution can be tested as in the case of viscose by determining Kw.

The neutralized solution is again filtered and NaCMC is precipitated by methanol. The purified sample is tested for D.S. Since this derivative is applied in the form of concentrated aqueous solutions e.g. for textile sizing or as paper binder , therefore it is necessary to determine the flow or rheological properties(such as structural viscosity) of these solutions.

V. EXOTIC RAW MATERIALS AS A SOURCE FOR DISSOLVING PULPS :

Exotic raw materials may be defined as those raw materials which are strange to the industry of dissolving pulp. In this respect all non-wood raw materials except reeds can be considered as exotic raw materials. Examples of non-wood raw materials which are abundant in many countries are sugar cane, bagasse and agricultural residues such as straws. A tremendous amount of research work has been done on non-wood plants and a huge number of articles have been published about this topic. However most of the articles suffer from the fact that they are restricted to pulping , bleaching and refining processes. Further investigations on the conversion of the obtained pulps to different cellulose derivatives are scanty. On the other hand , some abundant exotic raw materials as cotton stalks , palm leaves and corn cobs have been almost neglected in the literature regarding their use for dissolving pulps. In the present paper it is impossible to give a review of all articles about exotic raw materials. Only the

most important literature and the basic features of the subject will be discussed.

The present paper will be confined to straws , sugar cane bagasse , cotton stalks , palm leaves , and corn cobs. Reeds are also included in the present study due to similarities with several other exotic raw materials. It is around these materials that the author gained experience in the last twenty years. The study will concentrate on the problems of these raw materials as a source for production of dissolving pulps. In other words , the difficulties in preparation and purification of these pulps as well as technical difficulties during conversion of the obtained pulps into different cellulose derivatives will be stressed. Ways for more or less reducing these problems and difficulties are described or suggested.

In fact all raw materials considered in this paper are generally speaking characterized by a more heterogeneous anatomical structure than softwoods and hardwoods. Great differences in chemical composition and fine structure of cell types are encountered. For instance , epidermis cells which are found in non-wood raw materials contain much higher ash and silica content than other cell types. The differences between cell types is however not as much as that in the case of flax where

each of the bast fiber portion and the woody portion has to be pulped separately. But anyhow heteroginity in structure of most exotic raw materials cause several difficulties for production of dissolving pulps as will be shown later.

A general characteristic of these raw materials is their overall high ash content if compared to soft or hardwoods. In some cases more than 50 % of the ash ia made of silica. Straws and bagasse possess lower lignin than woods. It is easy to obtain pulps of high alph-cellulose from straws and bagasse by applying more reduced pulping conditions than those used for wood. Nevertheless it is difficult to reduce the amount of silica to values permissible for dissolving pulps. A more or less sufficient reduction of silica usually takes place at the cost of the pulp yield.

Practically all pulping processes practiced in manufacture of dissolving pulps from wood have been tried in the case of exotic raw materials. Also specific pulping processes such as Pomilio-Celdecor process have been developed for non-wood raw materials. Different bleaching and refining processes have also been applied. Optimum conditions for production of pulp with best purity have been given. However this depends upon variety , location , and storage. Most of the articles demonstrated that Prehydrolysis-sulfate is the most suitable method for preparation of dissolving

pulps from exotic materials.

The raw materials considered in the present paper although they share some characteristics yet they vary in others. Therefore they are classified here in groups according to common specific problems as far as dissolving pulp is concerned. Each group will be discussed in detail as follows:-

1. Viscose grade pulps :

Reeds :

Simionescu (13) in his book on reeds gave a review of all articles published on this subject till 1965. Among reeds , Arundo Donax has been used for some times in Italy for production of viscose pulps. Calcium bisulfite process was applied to arundo , using pulping conditions similar to conditions used for spruce (1). Another abundant reed is Phragmites Communis. In phragmites the leaves constitutes 18 % of the whole raw material while in Arundo leaf content is about 10 %. Leaves contain much higher ash and silica than stems. Therefore it is recommended to remove the leaves before pulping. The ash in Arundo stems (an Egyptian species) is about 4.5 %. Silica in ash is 40 %. Deleaved Egyptian phragmites contains about 6.9 % ash of which 25 % is silica. Unbleached pulps obtained from reeds by the bisulfite methode contain still high ash and silica. By refining with sodium hydroxide before or during bleaching it is possible

to obtain dissolving pulps with low silica.

It is worth mentioning that other non-wood raw materials such as bagasse and wheat straw contain less silica than reeds. However when pulped by the bisulfite process these raw materials deliver pulps in which the silica cannot be reduced to permissible values even after intensive alkali refining . This demonstrates that silica is found in different forms in different raw materials. This could be a point of further research.

In other investigations in this laboratory it has been shown that reeds can be well cooked by the calcium bisulfite process under much shorter pulping cycles than those used for wood (14). A total pulping cycle of five hours was sufficient to obtain well cooked pulp of high alpha-cellulose. Since reduction of silica in the unbleached bisulfite pulps necessitates an intensive alkali refining before or during bleaching , therefore in one experiment the pulping chemical ratio as well as pulping cycle were both reduced. Practically speaking a semichemical pulp of 53 % yield and low alpha-cellulose was obtained. However after alkali refining followed by bleaching a high alpha-cellulose content of 94.7 % was reached. The results are shown in Table 2. In other experiments refining was done in the second stage of bleaching by raising the concentration of sodium hydroxide in this alkali

Table 2

		Pulp 1						Pulp 2	
Conditions of Sulfite pulping	Free SO_2	25%						6%	
	Combined SO_2	9%						4%	
Pulp analysis	Yield %	43.1						53.1	
	Pentosan %	11.88						15.68	
	Lignin %	5.28						12.63	
	Ash %	3.38						3.61	
Conditions of hot refining of pulps	NaOH conc./ 100 gr. pulp	8 Alcoholic	16 Alcoholic	24 Alcoholic	8 Aquous	16 Aquous	24 Aquous	16 Aquous	24 Aquous
	Liquor ratio	5	5	5	5	10	10	10	10
	Maximum temperature °c	125	125	125	125	125	125	125	125
	Time at max. temp. h.	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Yield %		36.50	34.60	32.90	36.70	33.70	25.00	34.80	30.20
Pentosan %		6.01	6.83	7.26	4.14	3.27	4.13	5.39	5.41
Ash %		3.17	1.42	0.61	3.20	0.28	0.24	0.29	0.23
Alpha cellulose %		93.80	94.30	94.10	94.80	94.90	-	94.70	-

washing stage. Also successful results were obtained. In further experiments the calcium was replaced by other cations but the pulping conditions were held constant and equaled those used for producing the calcium bisulfite pulp No.1 in Table 2. The alkali refining was done as the second stage of bleaching by using 16 % NaOH (based on pulp) for 2½ hours at 95 °C. The results are given in Table 3. For the sake of comparison two prehydrolysis-sulfate cooks were carried out. For preparing pulp No.8 , 6 % H_2SO_4 based on raw material was used in the prehydrolysis step. Liquor ratio was 7:1 , maximum temperature 125 °C. and duration at maximum temperature 170 minutes. In the pulping process , 21.5 % NaOH and 5.3 % Na_2S (based on prehydrolysed material) were used at a liquor ratio of 5:1. Maximum temperature was 160 °C. and pulping period at maximum temperature was 3 hours. The natural chlorine requirement for the sulfate pulps was about 1% while it amounted to about 4% in short cycle bisulfite pulps and about 2-5 % in long cycle bisulfite pulps. From Table 3 it is evident that the prehydrolysis-sulfate process deliver pulps with lowest ash and silica. However Kw of the viscoses obtained from several bisulfite pulps were not inferior. This again demonstrates the absence of a clear-cut relationship between pulp analytical data and viscose Kw. It is worthwhile to mention that Kw of viscoses obtained from

Table 3: Analytical data and viscose filterability of bleached pulps

Pulp No.		1	2	3	4	5	6	7	8	9
Pulping process		Sodium bisulfite (short cycle)	Amm. bisulfite (short cycle)	Magnesium bisulfite (short cycle)	Calcium bisulfite (short cycle)	Calcium bisulfite (long cycle)	Calcium bisulfite (long cycle)	Calcium bisulfite (long cycle)	Prehydrolysis sulfate	Prehydrolysis sulfate
Yield	%	34.750	31.290	32.480	32,830	31.740	33.720	31.810	28.120	35.670
Alpha cellulose	%	96.630	95.380	95.750	96.590	96.150	95.740	95.130	97.680	92.610
Pentosan	%	4.580	5.850	5.170	4.810	4.780	7.150	7.240	2.630	3.920
D.P.		895	870	920	840	910	895	-	845	860
Ash	%	0.110	0.080	0.080	0.100	0.150	0.460	0.079	0.041	0.048
Silica	%	0.063	0.056	0.048	0.050	0.120	0.320	-	0.018	-
M.R.V.	%	98.260	78.420	87.360	89.680	71.700	89.280	90.340	80.700	85.720
Reactivity as insol. residue	%	74.420	61.400	74.030	85.070	69.560	60.890	59.780	-	86.920
Kw		194	182	143	258	289	367	228	228	196

Pulp 6 is refined before bleaching with 16% alcohol. NaOH at 125°C., Pulp 7 as 6 but 24% alcohol., NaOH

Other bisulfite pulps are refined during bleaching with 16% aq. NaOH at 95°C.

average grade commercial hardwood dissolving pulps under same testing conditions amounted to 200.
Summing up Arundo donax is one of the few non-wood materials which give suitable viscose pulps by the bisulfite as well as by the prehydrolysis-sulfate method.

In the fore going experiments reeds were deleaved before pulping. It is known that the objectionable high ash and silica content in leaves is almost confined to the epidermis layers on the surface of the leaf. Other cell types of the leaves would not be objectionable for dissolving pulps. It is difficult to separate the epidermis cells from other cells e.g. O-fiber or fines such as parenchyma cells and to study the behaviour of each type alone. However it was noticed that after hydrolysis of reeds (as well as straws), the epidermis cells which form the superficial layers of the leaves are more or less dissociated from the body of the leaf and split easily upon mechanical stirring to small particles which can be removed through screening (15). The whole process can be done in a hydra-pulper with false bottom. In this way most of the epidermis cells of the leaves can be eliminated while other cell types are retained to be utilized in pulping. After pulping of the prehydrolysed Arundo which has been screened

after pr hydrolysis , the ash and silica was still higher than in the case of pulps obtained from completely deleaved material (i.e. stems) and the Kw of the viscose was respectively inferior (compare experiment No.6 and No.7 in Table 4) (15). In the case of phragmites communis , screening after prehydrolysis of the whole plant (stems + leaves) led to a pulp with almost same ash and silica content as that obtained from stems alone but with much better viscose filterability (compare experiment No.4 and No.2). This proves that fines (other than epidermis) improve the filterability of viscose. Pulp No. 5 was once screened before bleaching to remove the O-fiber fraction (experiment No.3) and Kw of its viscose determined. The Kw decreased due to this treatment. Again it is seen that as far as the epidermis cells are removed to sufficiently reduce ash and silica in pulp , other O-fiber fractions or fines do not deteriorate pulp quality. They even improve the filterability of viscose tremendously. Of course the presence of more O-fiber fraction in the pulp increases the degree of heterogenity of the pulp. As mentioned before it is believed that the more the heterogenity of the pulp the lower will be its suitability for cellulose conversions. However in this specific case it is shown that the presence of more fines (except epidermis cells) does improve viscose filterability. It

Table 4

Exp. number	1	2	3	4	5	6	7
Pulp number	4	5	6	7	8	13	14
Pulp (raw material)	Phr. comm. stems and leaves	As exp. 1 but screened after prehydrolysis	As exp. 2 but again screened after pulping	Phr. comm. stems	Phr. comm. stems screened after pulping	Ar. don. stems and leaves screened after prehydrolysis	Ar. don. stems
Alpha cellulose %	95.920	96.630	-	96.230	97.790	97.190	97.680
Pentosan %	2.310	2.180	-	2.370	2.280	2.880	2.630
D.P.	810	830	-	850	830	870	845
Ash %	0.190	0.048	-	0.046	0.058	0.085	0.041
Silica %	0.143	0.021	-	0.019	-	0.038	0.018
Kw	520	194	386	467	561	390	212

might be that such fines give viscoses with better state of solutions. This point however needs further research work to be clarified.

Straws :

In wheat straw the leaves amount to about 35 % of the whole straw. In rice straw the percentage of leaves is as high as 65 % of the whole raw material . In Egyptain wheat straw the ash and silica contents are about 6 and 2.5 % respectively in stems and 15 % and 7 % respectively in leaves. In rice straw the stems contain 13 % ash and 8 % silica while leaves contain 22 % ash and 17 % silica. In this respect the leaf blade contains considerablely higher ash and silica than the leaf sheath. It becomes evident that the leaves have to be removed from straws before pulping so as to obtain pulps with low ash and silica contents. Jayme obtained pulps from deleaved wheat straw which were suitable for acetate grade. However there is no mechanical device which could deleave straws completely. Furthermore deleaving of straws - in contrast to reeds - causes about 50 % loss of the raw material. In one of our papers this problem has been practically solved by the technique described before in the case of reeds. In fact this technique was first developed by us for straws and then applied to reeds. After prehydrolysis of straw , a considerable

part of the epidermis cells were removed by screening before pulping. The leaf blades become brittle upon hydrolysis and especially the surface layer of epidermis cells dissociate to small particles which can be easily screened. The removal of only 8 % of hydrolysed material which is equivalent to 12 % of the whole raw material resulted in an enormous reduction of ash and silica in pulps. However application of conventional conditions of alkali pulping to the hydrolysed straw especially rice straw delivered pulps with higher ash and silica than permissible for viscose pulps. Therefore a systematic study of pulping conditions was done. It was found that silica redeposits continually in great amounts during the early stages of pulping while lignin is still being more or less solublized. Therefore it is necessary to apply very short pumping cycles. Even pulping for 5 minutes at maximum temperature could be sufficient to deliver high alpha-cellulose pulps with low ash and silica content and which can be easily bleached (16). In further experiments alkali refining was instensified and the silica was reduced to 0.05 % a value similar to that for purified cotton linters. The Kw of the viscose prepared from this pulp is shown in Table 5 (17). It becomes evident that it is possible to obtain suitable viscose

Table 5

Raw material	Corn cobs	Palm leaves	Rice straw	Rice straw	Rice straw	Cottor stalks	Softwood
Pulp No.	1	2	3	4	5	6	7
Alpha cellulose %	93.000	93.400	94.000	93.500	94.100	92.100	92.500
Ash %	0.096	0.108	0.117	0.115	0.126	0.163	0.058
Silica %	-	-	0.051	0.051	0.064	-	0.006
D.P.	625	600	660	580	660	750	650
Viscose viscosity sec.	45	55	56	44	47	56	50
Kw of viscose	120	200	316	240	460	384	235

pulps from practically the most inferior non-wood raw materials i.e, rice straw. Of course the yield of such pulps are lower than in case of woods. Bisulfite pulping was insuccessful for straws.

Sugar Cane Bagasse :

Sugar cane bagasse consists , generally speaking , of two fractions , fibers and pith. The pith constitutes about 25 % of the raw material and contains somewhat higher ash and silica than the fibers. There are sevearl methods which have been developed for the removal of pith. To discuss these methods in details is out of the scope of this paper. Depithing is usually applied to bagasse in the wet state or in slurry. Depithing is necessary for paper making since if the pith exceeds a certain percentage in the pulp then it will deteriorate paper strength. For dissolving pulps , it is necessary of course to remove the silica-rich cells but it is not necessary that the pulp be of fibrous nature. In fact it has been shown that it might be sufficient - for dissolving pulp preparation - to remove only the loose pith cells which are contaminated with dirt and dust. Dry cleaning of bagasse by compressed air removes about 5 % of the raw material. Screening the bagasse after hydrolysis to remove again about 5 % based on raw material is sufficient to

reduce the ash content (18). Further depithing does not result in any improvement in pulp quality. The prehydrolysis-sulfate method when applied to bagasse delivers pulps of high alpha-cellulose content and of viscose filterability more or less comparable to reeds. Bagasse is an easily pulpable material. It can be even pulped at 100°C. to give high alpha-cellulose pulps (18). Although bagasse contains lower ash and silica than reeds yet it is difficult to obtain suitable pulps from it by the bisulfite method which is successful in the case of reeds.

Cotton Stalks :

The bark makes up about 20 % of cotton stalks. Cotton stalks also contain a considerable amount of pith. Due to the thin and branched nature of cotton stalks it is difficult to remove the bark totally by mechanical means. Even those debarking devices which are extra designed for cotton stalks leave about 8 % bark (based on raw material) still attached to the stalks. If the rest of the bark is manually removed , cotton stalks can be easily pulped by the bisulfite process by applying conditions similar to those used for reeds as before mentioned. The obtained pulps can be easily bleached to high alpha-cellulose content and high brightness. However the presence of residues of bark interfer with bisulfite pulping.

Bark parts do not desintegrate completely during pulping and many very thin tissues of big size and dark colour remain in the pulp and are difficult to be removed by screening or centricleaning. On the other hand , the prehydrolysis-sulfate method leads to complete desintegration of the residual bark and considerable dissolution of the coloured matter of the bark. Thus the bast fibers in the bark are easily released and contribute to the pulp. Practically speaking the undebarked cotton stalks can be used in the prehydrolysis sulfate pulping ; but in this case bleaching is too difficult. In Table 5 , properties of a prehydrolysis-sulfate pulp are given(17).

Palm Leaves :

The palm leaf consists of middle rib and leaflets. The middle rib contains somewhat higher cellulose but lower ash than the leaflets. Ash in the middle rib is about 5.8 % while in leaflets it amounts to 8.7 % in an Egyptian species. Average conditions of prehydrolysis-sulfate pulping delivered pulps of less than 88 % alpha-cellulose and considerably high ash content from leaflets ; but better pulps were obtained from middle ribs. Therefore the leaflets have to be discarded as a source for dissolving pulps (19). Middle ribs give pulps of suitable analytical data and the viscose obtained therefrom possessed Kw comparable to that obtained from softwood pulps (Table 5).

Corn Cobs :

Corn cobs possess the lowest ash content among the non-wood materials discussed in this paper. The ash is about 1.2 %. Therefore it does not cause any problem , but corn cobs contain somewhat higher pentosans than palm leaves or cotton stalks. corn cobs can be pulped by the prehydrolysis-sulfate method under more reduced conditions than all other agricultural residues. After prehydrolysis with 4 % H_2SO_4 (On raw material) at 120 °C. for 3 hours , it was sufficient to use 15 % NaOH (on prehydrolysed material) for pulping at 160 °C. for 1 hour. The natural chlorine requirement of the obtained pulp was 1.04 %. The Kw of the obtained viscose was lower than values for viscoses obtained from all other pulps even softwood pulp (See table 5). Since corn cobs pulps consist almost of O-fiber fraction , it becomes evident that the fines as far as they are not rich in ash and silica could deliver better viscoses han that obtained from fibers. However many difficulties were encountered through washing of corn cobs pulps since they are powdery in nature. Also it is known that in some processes fines could lead to troubles during pressing of alkali cellulose.

2. Acetate grade pulp :

Acetate grade pulps require the highest purity among dissolving pulps. In the present work only sugar cane bagasse

and flax bast fibers (residues of of particle board mills) were investigated. It is known that flax bast fibers due to their relatively high cellulose content , can be purified under reduced conditions and give high yields. In the case of sugar cane bagasse several prehydrolysis , pulping and refining experiments were carried out using an industrially depithed material. The yields ranged from 31-36 % , Hemicelluloses from 1.3-3 % , Alpha-cellulose from 96-98 % , and the ash was lower than 0.10 %. The initial and final turbidity of the acetylating mixtures in case of bagasse pulps were in all cases lower than turbidities of acetylating mixtures in case of a commercial acetate-grade cotton linters samples despite similar D.P. and carboxyl content. However the undissolved residue was higher in the case of mixtures obtained from bagasse pulps. In Table 6 , the properties of the diacetates are given (20). It is clear that only bagasse pulp No.5 is competitive with commercial cotton linters except higher ash content of the acet te. This bagass : pulp was prepared under the following conditions :-

Prehydrolysis was done with 2.5 % H_2SO_4 (On raw mwterial) at 120°C for 2 hours. Pulping was done with 23 % NaOH (On hydrolysed material) at 165°C. for 2½ hours. Bleaching was carried out in 4 stages:- Chlorination with 1.8 % chlorine (based on pulp) , alkali treatment with 18 % NaOH at 50°C. for 1.5 hours, then followed a mild hypochlorite and chlorite stages.

Table 6 : Analysis of the diacetate

Raw material	Pulp No.	Acetyl content	Charring point °C	Stability as liberated Ac OH%	D.P.	Ash %	Solubility in acetone%
Bagasse	3	36.01	195.0	0.845	104	0.191	99.5
	4	36.85	218.0	0.304	139	0.163	99.2
	5	39.78	225.5	0.245	183	0.185	99.9
	6	36.77	211.5	0.248	132	0.159	99.6
	7	37.42	210.5	0.268	125	0.185	99.6
Flax	9	39.57	229.0	0.282	206	0.152	99.8
	10	40.36	233.0	0.228	191	0.195	99.5
	11	40.00	229.0	0.301	183	0.182	99.8
Commercial cotton linters	-		219.5	0.414	183	0.056	99.9

Flax pulps in general gave diacetate of better properties than those from bagasse.

3. Nitrate grade pulps :

As mentioned before if the cellulose nitrate is not intended to be used for dissolving and regeneration purposes , more ash can be tolerated in the pulp than in the case of pulps of acetate grade , as far as the ash does not lower the stability of the nitrate . Therefore non-wood raw material could be suitable for this purpose. Preliminary experiments showed that cotton stalks and bagasse could deliver cellulose nitrates of fair stability.

4. Ether grade pulps :

Ether grade pulps should be of high purity. The use of several non-wood raw materials for this purpose would be questionable. However for the specific case of Na CMC , criteria similar to those of average grade viscose pulps are sufficient. This water-soluble derivative can be even used in a crude state for some purposes as mentioned before.

Investigations on several non-wood raw materials showed that by varying pulping conditions , the reactivity of pulps towards carboxymethylation can be easily changed (21). Thus conditions for optimum reactivity could be easily adjusted. It was noticed that most non-wood pulps require higher D.S. than wood pulps to

achieve complete water solubility of the NaCMC. The flow properties of the obtained solutions depend upon many factors. Beside the raw material used , the pulping cycle played a considerable role (22). In other words the requested flow properties can be more or less adjusted by varying pulping and refining conditions.

CONCLUSIONS

Bisulfite pulping suits a few number of exotic raw materials. It leads to pulps with high ash and silica contents in most cases. Further intensive alkali refining fails to reduce the silica sufficiently. Traces of bark in raw material such as in the case of cotton stalks cause difficulties in bisulfite pulping. Bark parts do not desintegrate easily and give dark unbleachable thin tissues which cannot be easily removed by screeing or centricleaning.

Among all pulping processes, the prehydrolysis-sulfate process is the most suitable for producing pulps from exotic raw materials. It is easy to obtain high alpha cellulose pulps by this process. The residual ash and silica are lower than in th case of bisul..ite pulps. However the contents of these impurities are usually still higher than permissible for the lowest grades of commercial wood pulps. Therefore it is necessary to remove plant portions rich in silica, completely or partially, before pulping. These portions are leaves in the case of reeds, leaf blades in case of straw, leaflets in case of palm leaves, and pith in case of sugar cane bagasse. Deleaving of reeds represents no problem. Leaves constitute only

10-18% of the whole raw material and can be totally and easily removed. In straws, on the other hand, leaves constitute 35-65% of the raw material; moreover there is no mechanical device for complete deleaving of straws. However, it was found that after prehydrolysis of straws, the epidermis surface layers split easily from the body of the leaf especially the blade. It is in these layers where the silica is concentrated. After mechanical stirring of the prehydrolysed leaves in water, the epidermis layers dissociate into small particle which can be easily removed by screening. The loss in yield due to this operation is only 12% (based on raw material) in the case of rice straw. This leads to an enormous reduction of ash and silica contents of pulps. A further reduction of silica can be affected by carefully adjusting pulping conditions. Silica shows a unique behaviour during pulping of raw materials. Silica dissolves very quickly in the early stages of pulping then redeposits on fibers at a great rate. By applying short pulping cycles the problem of silica redeposition can be solved. C-fiber fraction other than epidermis cells is usually poor in silica. Such fraction was found to improve viscose filterability in several cases. However this point needs further research.

In the case of bagasse it was also found that it is sufficient to remove a small fraction of the pith, namely only the loose fraction contaminated with dust and dirt. Another way leading to improvement of viscose filterability is by reducing the D.P. of the pulp during pulping and bleaching to an extent which eleminates the aging of alkali cellulose (23). This point also needs further research. Viscose additives might be helpful. Rayon filaments obtained from several non-wood raw materials were not bad.

It becomes evident that by taking several measures , it is possible to obtain suitable viscose grade pulps from almost all exotic raw materials. These pulps are equivalent to some commercial pulps. On the other hand it is difficult to obtain acetate, ether, or nitrate grade pulps from many exotic raw materials. It is extremely difficult to reduce the ash residues to values permissible for such grades. If such purification is achieved, it is usually at the cost of pulp yield. The diacetate obtained from most non-wood raw materials are inferior in quality to commercial samples. However pulps from non-wood raw materials could be suitable for cellulose nitrate manufactures for purposes where dissolution and regeneration of the nitrate is not practiced. For the specific ether, sod. carboxymethyl cellulose it is

not necessary to use pulps of high degree of purification. Accordingly exotic raw materials can also be utilized for this purpose.

Non-wood pulps in general are sensitive to drying. If not certain precautions are taken, the pulps could be passivated towards chemical reactions.

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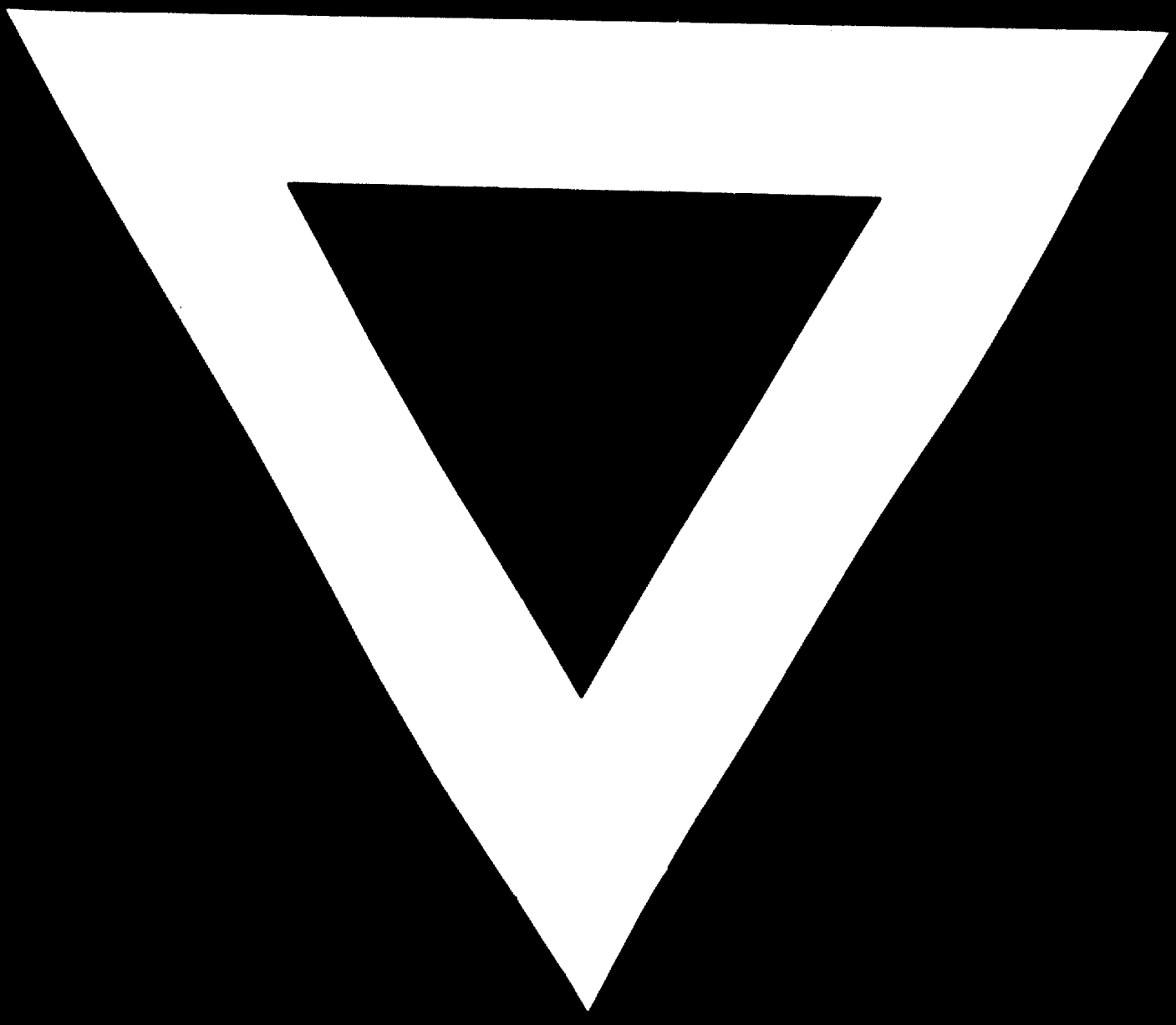

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