PROPERTIES OF LOCAL WASTE PAPERS

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ABSTRACT

Some physical and chemical properties of mixed waste papers collected in Uyo town had been investigated. The wastes consisted of papers of various shapes, grammage and colours depending on their application. A few were good water absorbent while many had low water absorbent capacity, the chemical additive present in the papers were the starch, rosin size and various fillers. Variation of starch in some of them was in the order coated paper > drawing paper > security paper > brail paper > writing paper, while newsprint contained no starch; the rosin content was in the order security paper > drawing paper > photography paper while filter paper contained no rosin size; residual lignin was found in newsprint, exercise book cover, computer paper and some tissues. The filler contents in the waste paper were: Cigarette paper - $CaCO_3$ (1.99%), $ZnSO_4$ (2.42%); Photography paper – $CaSO_4$ (2.71%); photocopying paper – $CaSO_4$ (3.44%); $ZnSO_4$ (2.16%); security paper – TiO_2 (0.004%), and wrapping paper – Al_2 $(SO_4)_3$ (0.05%). Refluxing of these waste papers in water and 1% NaOH removed most of the chemical additive thereby improving their water absorbent capacity and hence the base used in repulping waste papers into secondary fibres.

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INTRODUCTION

Paper is defined as a sheet of continuous web of material formed by the deposition of vegetable, mineral, animal or synthetic fibres or their mixtures with or without the addition of other substances, from a suspension in a liquid, vapour or gas in such a way that the fibres are intermeshed and bonded together (Grant, 1978).

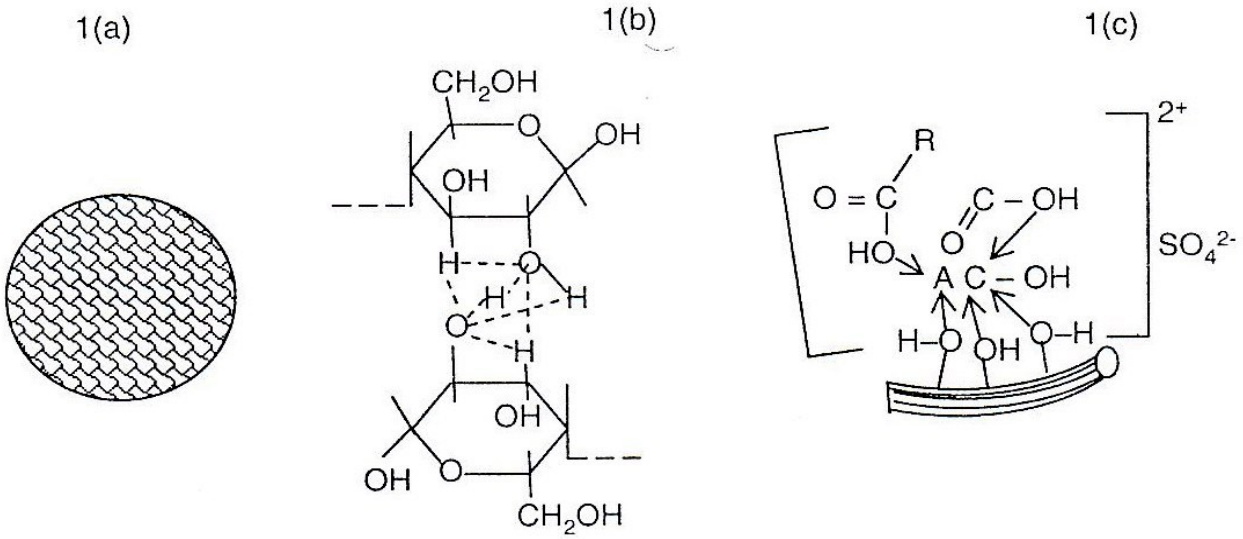


Fig. 1: Structure of paper

(a) Intermeshing of fibres in dry sheet of paper

(b) Hydrogen bonds in dry sheet of paper (O....H)

1(c) Al retaining rosin size on fibre.

Papers are chiefly used for writing, printing, drawing and painting purposes, they are used as security material for commercial exchange of goods and services; they also serve as filters and cleaners and as constructional material in the form of boards. Table 1 shows the paper consumption pattern in Nigeria from 1983 – 1992 (Federal Office of Statistics, Uyo).

Waste papers, on the other hand are those papers that have been discarded after their intended use because the information they contain are no more useful, examples are discarded examination answer scripts; or they are those papers that have not been formed to the required specification, i.e. "broke" which occur during paper manufacture; they are also those papers that have been badly damaged by insects or adverse weather conditions during storage.

Waste papers are of economic importance if they are recycled into secondary fibres for making new papers. Some secondary paper mills depend entirely on waste papers for their fibrous raw materials, especially in places e.g. Nigeria where there is no virgin pulp production. On the other hand if the waste papers are not properly collected they liter our homes and premises, and when burnt the increase smoke in the air will constitute air pollution and the carbon (iv) oxide and other gases from the pulp and paper additives may increase the acidity of the air leading to formation of acid rain which pollutes our environment.

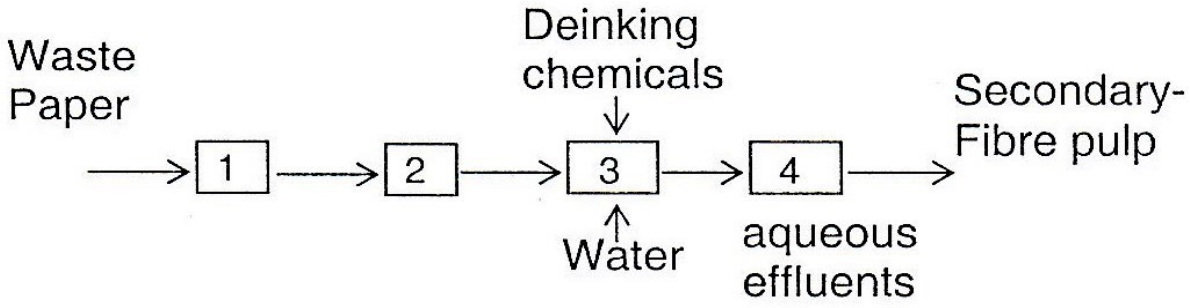
TABLE 1: PAPER CONSUMPTION IN NIGERIA FROM 1983 – 1992

YEAR	*QUANTITY IN METRIC TONNES
1983	144,788
1984	125,009
1985	204,970
1986	155,324
1987	469,186
1988	612,879
1989	887,793
1990	1,609,088
1991	1,247,587
1992	4,148,217
*1990	6,000,000

* Computed from the data obtained from the Federal Office of Statistics, Uyo.

* Estimate.

Secondary fibre pulp production from waste papers involves sorting of the waste papers into classes; removal and screening; cleaning involves deinking or removal of the chemical additives present in papers (see Fig. 1).



1. Sorting
2. Removal of contraries
3. Defibering deinking operations
4. Cleaning and screening

Fig. 1: Operations in Secondary Fibre Pulp Production

However, before one embarks on the secondary fibre pulp production there is need to know the non fibrous materials present in the waste papers and the mechanism of their retention in the sheet. This will enable one design a viable recycling system. Broadly non-fibrous materials associated with waste papers are:

(i) The contraries, consisting of the stapling pins, strings, the plastic materials (paper wrappings), file jacket clips and metal chains.

(ii) The chemical additives consisting of those chemicals e.g. starch, dyes, sizing agents (Fig. 1(c)), security agents and wet strength agents added to the stock during sheet formation and those acquired by the paper during use e.g. ink, adhesive; oil, and coatings; there are also inherent chemicals present in the fibres which may affect method of defibering; these are the lignin and resin acids which are always present in the ubleached mechanical pulps or semichemical pulps used in making some papers.

In this study both the chemical additives and the inherent chemicals were assessed and determined from some selected waste papers found in Uyo town; effect of extraction of these papers with organic solvents, water and

sodium hydroxide (1% NaOH) solution on the water absorbent capacity of the papers was also studied in order to assess the mechanism of retention of these chemicals on the sheets.

MATERIALS AND METHODS

Materials: A bag of mixed waste papers randomly collected from the University of Uyo Town Campus; Ikpa Road; printing, photocopying and duplicating houses and Uyo market was used in the experiment. The contraries were removed physically and the waste papers were sorted into classes.

2.2 METHODS

2.2.1 Determination of Grammage:

The representation of each class of waste, paper was cut into rectangular pieces of known length (1) and width (b) and weighed on a balance. The grammage in GSM (Gramme per square meter) was calculated (Dawe, 1939) from:

$$GSM = \frac{m}{1 \times b}$$

where m = mass of each piece of paper in gramme

1 = length in meter

b = width in meter

2.2.2 Determination of Moisture Content:

1g of each sample was weighed in air, dried in an oven at 105 ± 5°C for 24 hours and then cooled in a desicator to a constant weight. The moisture content was the determined by the difference expressed in percentage of the air dry paper (Browning, 1977).

2.2.3 Determination of water absorbent capacity:

3cm x 3cm samples were cut from each sample, and weighed in air. it was then put in a deinoized water in a beaker for 15 seconds; it was quickly removed and the excess water removed by pressing the paper on the side of the beaker and weighed immediately with a digital balance. The water absorbent capacity (A.C) was expressed in gramme of water absorbed per gramme of A.D paper.

Determination of Ash Content:

This was done according to the method described in the A.O.A.C 1975 by ashing 1.0g of each sample in a muffle furnace at a temperature of 525 ± 25°C.

Detection of Lignin:

Lignin was detected by addition of a solution of phloroglucinol in water, methanol and concentrated HCl to the paper. Violet-red colour gave positive test (Browning, 1977).

Detection and Determination of Starch:

The starch in paper samples was detected by developing a blue black colouration when a drop of potassium iodide – iodine (KI/I_2) solution was placed on the paper.

It was determined quantitatively by the use of spectrophotometer (spectronic 20) which measured the absorbence, of the KI/I_2 solution paper extract at 580nm (Browning, 1977).

Detection and Determination of Rosin size:

The rosin size in paper was detected when acotic anhydride extract of the paper sample in a test tube developed a rose-violet colour as a drop of conc. H_2SO_4 placed on the side of the tube touched the extract front. It was quantitatively determined by total extraction in acidified ethanol solution (Browning, 1977).

Solvent Extraction:

Successive extraction in soxhlet apparatus was carried out with the samples using the following solvents in the order chloroform, benzene, ethanol and water; direct extraction of the fresh samples with water alone was also carried out. The extracts were concentrated and standard tests for starch, rosin and lignin were carried out.

Water absorbent capacity measurement was also done for both the extracted and the unextracted samples.

Refluxing with 1%NaOH

Each sample was refluxed in 1%NaOH for 1 hour, the extracted papers were dried in air and the water absorbent capacity determined.

Detection and Determination of the Inorganic Additive (fillers) in Paper.

The trioxocarbonate (IV) – CO_3^{2-} ion was detected by production of effervescence when the paper was treated with 2MHCl, the gas forming milky coloured solution when bubbled through lime water.

The tetraoxosulphate (VI) – SO_4^{2-} ion was detected by treating the paper with dipotassium heptaoxo chromate (VI) ($K_2Cr_2O_7$) and 2MHCl, producing a colour change from orange to green.

The cations were detected from the ash by wet method as approved by A.O.A.C. 1975. Quantitatively they were determined by the use of Atomic Absorption Spectrophotometer (AAS).

RESULTS AND DISCUSSION

Available local waste papers: Table 2 shows the percentage composition of the mixed waste papers collected from Uyo for this study. Table 3 shows the grammage, moisture content and Ash content of the Waste Papers.

Table 2: Types of local Waste Papers, their Percentages and Sources

TYPE OF PAPER	QUANTITY	SOURCE
Draille paper	2	Market (bag)
Calendar paper	3	Household
Printed paper	20	University, printing houses, photocopying houses
Drawing paper	6	School
Writing paper	40	University, Schools, market, household.
Security paper	1	Bank
Unprinting paper	10	Printing, photocopying paper converting houses.
Photography paper	2	Photographers shop
Cigarette paper	1	Market
Brown wrapping paper	5	Market
Paper board	7	Market
Coated papers	3	University
	100	

Table 3: Grammage, Moisture and Ash Content of some Waste Paper

TYPE OF PAPER	GRAMMAGE G S M	M. C. %	ASH %
Brailler Paper	118.9	12.9	10.60
Calendar (coated)	123.3	12.8	19.6
Printed (news) Paper	60	9.1	0.4
Drawing (coated) Paper	6.7	6.7	9.7
Writing Paper	56.0	11.4	3.2
Security Paper	87.2	8.6	3.6
Unprinted Paper	55.6	10.8	4.5
Photography Paper	198.9	8.5	14.15
Cigarette Paper	17.8	5.6	22.6
Wrapping Paper	57.8	8.7	2.0
Coated Paper	80.4	10.3	20.4

The results showed that writing paper (40%) was the highest amount of waste paper collected, they were in the form of examination answer scripts from the university and schools. The next were the printed papers (20%) which were sourced from old books, letters, newspapers and officially discarded documents.

Generally, because of lack of big printing houses in Uyo direct entry waste papers, containing no ink or printing matter were not very high as is the case in big commercial cities.

The grammage; moisture and the ash content of the waste papers are shown in Table 3. Ash determines inorganic components in the paper, coated papers usually contain more inorganic components than unloaded papers, this is shown in the

ash content of coated calendar paper (19.6%) Braille paper (10.6%), drawing paper (9.7%), photography papers (14.15%) and the paper coated on both sides had 20.4%. Special application also determines the amount and type of filler added to a paper formulation, this case is illustrated in the cigarette paper, though a light paper of only 17.8 GSM it contained as much as 22.6% ash; usually in the form of calcium carbonate which slows down the rate of burning of the cigarette paper during smoking. The grammage of paper is made to suit its particular application while the m.c. of the paper indicates the equilibrium moisture content with respect to the atmospheric moisture at the ambient conditions. It determines the dimensional stability of the papers.

STARCH, ROSIN AND LIGNIN IN WASTE PAPER

The variation of starch in the paper was in the order coated paper (2.12%) > drawing paper (1.96%) > security paper (1.64%) > Braille paper (0.92%) > writing paper (0.85%) while newsprint contained no starch. Starch was also not detected in the wrapping paper and in other printing papers apart from the newsprints. Starch is used as bonding agent in paper, adhering the fibres and other paper additives together in the structure, it also provides a smooth writing surface and an easy means for the ink to be retained in the sheet.

Lignin was only present in the newsprint, the tissues, the brown wrapping papers and in the paper boards. The presence of lignin is an indication that much chemicals must be used in the repulping of waste papers if white secondary fibres are to be produced. In fact waste papers that contain a lot of lignin are not economically suitable for recycling because they will consume much pulping and bleaching chemicals and at the end still retain specks or stickies on the finished product, as found in many tissues produced by many inferior tissue producing mills using waste newsprints in various forms as their raw material input without passing the recycled pulp through very effective cleaning systems.

Rosin, usually in the form of the paper makers rosin was highest in the security paper (4%): others were: drawing paper (3%) and photography paper (2%). All other papers were also sized to various degrees depending on their use. It is necessary to size paper in order to control water penetrating into the paper at normal atmospheric conditions. Sizing improves stability of the paper, however to repulp the waste paper rosin must be removed with some chemicals. Rosin, although retained with the aid of hydrated aluminium sulphate ($Al_2(SO_4)_3.109H_2O$) also serves as the adhesive medium for other paper additives.

INORGANIC COMPONENTS (FILLERS)

Table 4: Inorganic component (Fillers) present in some of the Waste Papers.

Type of Paper	% Inorganic Components (Filler)				
	$CaCO_3$	$CaSO_4$	$ZnSO_4$	TiO_2	$Al_2(SO_4)_3$
Cigarette paper	1.99	N.D	2.42	N.D	N.D
Photographic	N.D	2.71	N.D	N.D	N.D
Photocopying	N.D	3.44	2.16	N.D	N.D
Security	N.D	N.D	N.D	.004	N.D
Wrapping	N.D	N.D	N.D	N.D	0.05%

Inorganic components (fillers) found in some of the waste papers are shown in Table 4. Photocopying paper contained the highest amount of the fillers so as to provide enough opacity thereby preventing see – through when materials are photocopied on the paper. It makes it possible for the two sides of the paper to be copied upon. Inorganic components also decrease the strength properties of paper, hence both the security and wrapping papers which require high strength properties contained very low amount of the inorganic components (Britt, 1980).

SOLVENT EXTRACTION AND THE WATER ABSORBENT CAPACITY OF THE EXTRACTED SHEETS

Two paper selected for these tests were the coated paper and the newsprint. The result is shown in Table 5.

Extraction of paper with the given solvents increased the water absorbent capacity (A.C.) compared with the A.C. of the unextracted samples, except in the case of benzene and the coated paper where there must have been a problem of penetration of the solvent (water) into the sheet because of the surface coating. There was no significant difference on water absorbent capacity of the solvent extracted samples before water treatment and the direct water extracted samples. Tests on the extracted residue of the white coated paper revealed the presence of rosin in the ethanol extract and starch in the water extract for the newsprint, the ethanol and chloroform extracted residue gave positive tests for rosin; lignin test on the extracted newsprint was also positive.

Table 5: Water Absorbent capacity of extracted Waste Papers

SOLVENT SYSTEM	WATER ABSORANT CAPACITY (g/g)	
	White coated paper	Newsprint
Unextracted sample	.29	1.50
Chloroform	0.38	1.81
Benzene	0.29	1.89
Ethanol	0.36	1.92
Water	0.96	1.93
Direct extraction with only water	0.95	1.99
Refluxing with 1% NaOH alone	0.07	1.1

In all cases in which rosin and starch were present in the unextracted samples, these additives were also retained on the extracted sheets indicating that mechanism of retention might not have been due to physical adhesive forces only.

It was also interesting to observe that after refluxing the extracted sheets in 1% NaOH solution the sheets became harder sized than the unextracted samples whereas it wasn't sized if treated with water first, disintegrated and refluxed in 1% NaOH solution. This may be explained by the fact that NaOH reacted

with the rosin still present on the surface of the extracted sheets to form rosin soaps which then distributed themselves and filled up the openings between the fibres in the paper thereby rendering it hard sized. The implication here is that, since penetration of water into the paper web is necessary for effective defibering, waste papers should be soaked in water first before disintegration; thereafter they should be treated with sodium hydroxide which is the major chemical for removing the inks, the rosin, the lignin and other colouring matters by hydrolysis, thereby separating the fibres. Hydrolysis with NaOH breaks down any possible bonding between the chemical additives and the cellulosic fibres in the paper. Washing, centrifuging and screening remove the soluble products and heavier inorganic components, leaving, clean secondary fibres for re-use.

CONCLUSION

The local waste papers found in Uyo municipality are of mixed waste type. There is no effort to sort them into classes by the people.

In this study the major organic and inorganic components of waste paper were determined. These were the lignin in unbleached papers, rosin and starch in sized papers; and

coloured matter in dyed papers; inorganic components present included calcium carbonate and zinc sulphate in cigarette papers; calcium sulphate in photocopying papers; titanium dioxide in security papers and aluminium sulphate in the wrapping papers; each added component depended on the intended use of the papers.

Extraction of these papers with organic solvents did not disintegrate the paper or decrease the degree of sizing significantly; direct treatment with water followed by mild sodium hydroxide solution easily disintegrated and decreased the degree of sizing, hence these later systems should be used in defibering waste papers in order to produce clean, easily disintegrated secondary fibre pulp.

REFERENCES

A. O. A. C. (1975) Association of Official Analytical Chemistry. Official Methods of Analysis, 12th ed Benjamin Franklin Station, Washington D.C.

Britt, K. W. (1980) (ed) Handbook of Pulp and Paper Technology, 2nd ed.; Von Nostrand New York.

Browning, B. L. (1977). Analysis of Paper 2nd ed., Marcel Dekker Inc. New York. P. 133 – 153.

Dawe, E. A. 91939) Wood Consumption 3rd ed., Sampson Law Magton and Co. Ltd; London P. 536 – 537.

Grant, J. H. Young, J. H. Watson, B. G. (1978) Paper and Paper Board Manufacture 3rd ed. British Paper and Board Federation, London, P. 25 – 39, 137 – 165; 185 – 213.