IPPTA

Silver Jubilee International Sem[illegible] & Workshop
Appropriate Technologies For Pul[illegible] aper Manufacture
In Developing Countries.

New Delhi - 1989

TECHNOLOGICAL DEVELOPMENTS IN DEINKING OF WASTE PAPERS

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Abstract

The Indian Paper Industry uses only about 18-20% waste paper recycled furnishes in various grades e.g. News Print, Writing and Printing paper and Boards and Packaging media, as compared to Japan 45%, Denmark 65%, Germany 43% etc.

However, due to heavy deforestation, Paper Mills are now forced to increase use of Agrowastes as well as recycled waste papers. This effort calls for stremlining our available experience and Technology know-how for two important aspects of waste paper processing viz.:

a) Physical and technical characteristics of waste papers.

b) deinking and processing Technology. These two aspects are dealt with in some details in the following paper.

Introduction

The Indian Paper Industry uses only about 18-20% waste paper recycled furnishes in various grades e. g. News print, Writing and Printing paper and Boards and Packaging media, as compared to Japan 45% Denmark 65% Germany 43% etc. However, due to heavy deforestation, Paper Mills ar now forced to increase use of Agrowastes as well as recycled waste papeprs.

This effort calls for streamlining our available experience and Technology know-how for two important aspects of waste paper processing viz.

a) Physical and technical characteristics of waste papers.
b) Deinking and processing technology.

These two aspects are dealt with in some details in the following paper. Other equally important aspects which also require careful consideration are :

a Historical back ground and Technological advances in Deinking chemistry.
b Characteristics of Printing Ink formulations and their important constituents and
c The physico chemical meachanisms of Ink dispersions, suspensions removal and washing stages.

Finally, an attempt has been made to compile the available information for recommending a suitable Deinking Formulation for those who wish to develop Deinking Chemical Indigeneously.

Waste Paper Characteristics & Statistics

Recent statistics by FAO and other agencies indicate that while quality papers are expected to use only approx. 6–8% recycled waste furnish by 1990. nearly 40–41% furnish of waste papers will be used for Board and Packaging quality papers[1]. Since these varieties use predominently Letter Records and other types of medium – Low grade waste papers, their subsequent pulping and deinking processes assume great importanc. In India, technological understanding and available information on Deinking of waste papers is in the initial stages and it is necessary to understand and various formulations and processes developed through the years for coloured waste removal/dispersions.

Some data on present consumption pattern of waste paper in India and projections for 1990 are shown in Table–1.

Deinking Technology & Formulations

Early Attempts :

The subject of waste paper recycling has attracted world wide attention and as a result, the First conference on R & D efforts made by the EEC Countries was held in February 1982, followed by European Paper Industry Confederation Conference in June 1982 (CEPAC) and the International recycling Association Conference in October 1982[2]. Important Highlights of these Conferences are :

a Development of easily dispersible and water soluble Adhesives used for binding of Directories etc. in Germany.

b Huber West Germany have developed special printing inks which are easily deinked in subsequent pulping operations.

c While the letter press printing inks and Roto gravure inks are easy to disperse subsequently, offset printing inks are difficult to disperse and deink, probably due to the presence of Alkyd Resins in the ink formulations.

d A combined process of Flotation technique followed by washing is more effective in ink removal and also lowering of Loading ratio.

e Effective removal of "stickies" is not satisfactory inspite of various efforts by pioneering companies and R & D Laboratories such as Reverse Cyclonic Cleaning and Fibre fraction.

As a class the "Sticky" contaminents contain–

a Offset and other printed inks, drying oils and carriers.

b Waxes Bitumen etc. which adhere to the waste papers.

c Colour impurities and Laminated plastics etc.

Of these, only waxes and Bitumen respond to the 'Hot Melt' process of cleaning.

Solvent Systems

Normal drycleaning solvents have been used as early as 1930's with aqueous emulsions quite effectively. However a complete 'Dry Cleaning' process similar to that used for Textiles was tried out by the Riverside Paper Corporation U.S.A. using conventional solvents such as Aceotone, Toluene etc.[3] These data are presented in Table–II. The solvents were first tried on printed Brochures having **Lithographic Offset Printing Inks.** After shaking in jars, the waste papers were pulped and standard handsheets were prepared. These show very effective deinking levels e.g.

Acctone	– 80% brightness
Toluene	- 79% brightness
Perchlore Elthylene	- 74% brightness
Isopropanol	- 70% brightness

in another study an arbitrary solvent mixture was prepared using

Acctone	- 50% Vol.
Perchlore Elthylene	- 35% Vol.
Isopropanol	- 14% Vol.
Water	- 1% Vol.
Triton X–100	- 0.4% Vol.

In most cases, brightness levels of 90% and above were observed after the Drycleaing operation and contained coloured waste papers of Rotogravure Offset Litho graphic as well as Letter press inks from a variety of Printed books, magazines and coloured labels.

Advantages and Disadvantages of the Solvent Drycleaning Process

While there are many attractive features of the solvent processing, the main inhibiting factor seems to be an unwillingness on the paper mill technologists to adopt to a new process which involves some risk and demands higher efficiencies all around.

Advantages

1. Most ink vehicles e.g. Oils resins and varnishes are effectively removed. Thus Caustic soda is not required.
2. Minimizes large volumes of coloured contaminated waste waters. Cooling water used for solvent recovery can be recycled.
3. Waste papers after treatment are well preserved since there is hardly any defibration. Hence use of higher consistancies can be made.
4. The papers after treatment are in a dry state and can be baled readily.
5. Shrinkage is hardly 5–10%. Inks, Pigment and vehicles are effectively removed, while the papers are almost intact.
6. Practically all varieties of coloured/printed waste papers can be effectively cleared.
7. The waste coloured sludge after solvent recovery is a compact semi dry mass and can be disposed off easily.
8. "Stickies" such as waxes, Bitumen and some plastics also are effectively removed.
9. Even small size plants of 25/100 tonnes per day capacity can be economically run.

Disadvantages

1. Solvents being expensive the recovery systems demand high efficiencies (98 + % overall).
2. Some solvents are Toxic and some are inflammable. Hence health hazards are present.
3. Sorting of waste papers prior to solvent processing is still necessary since only printed/coloured waste papers should be fed to the system, otherwise the process may use additional solvents for non essential/non coloured contaminents.
4. There is an inherent resistance for paper mill personell to adopt to a new technology.

Important Characteristics of Printing Inks

With the advancement of modern high speed printing machines the pigment/ink formulations have also undergone dramatic changes and in order to achieve proper deinking of these coloured wastes a careful look at some important physico-chemical properties of these formulations is necessary.

In addition the manufacture of **Carbon Less** papers is also an important advancement and should be carefully noted. Tables II, III and IV show the important components of heatset ink formulations. The average single film thickness of the three major printing processes are–

Letter press– 4–6 UM

Litho offset– 1.5–3 UM

Rato gravure – 3–12 UM

Averaging these figures, roughly 2–5% of ink requires to be removed or approx. 15–50 kgs/per ton is the ink/binder load for processing.

Ink Drying Methods

The four princeple techniques/process of ink drying are Absorption, evaportion, Oxidation and radiation curing/heat polymerisation.

Absorption

In this process, the ink in effect does not dry but is absorbed through a 'Wick' action e.g. News prints. These formulations contain mostly Hydrocarbon and the seperation of pigment is through emulsification/mechanical removal.

Evaporation

Both letter press and offset type ink formulations as well as Rotogravure ink which are used in magazine publications belong to this class. Heat set vehicles are Metal resinates, Rosin Esters etc. As shown in Table III, the functionally modified Hydrocarbon resins are replacing rosin esters in many formulations.

Oxidation

These inks are mainly used in Litho offset printing on most packaging materials. The main constituents are binders which under-go oxidation/drying e.g. Oil modified Alkyed resins, Rosin esters and varnishes. These resins produce polymeric films which are not easily solubilized by the deinking solvents.

Radiation Curing

Ultraviolet curing inks contain Acrylic copolymers which cross link and form tough films which really do not contain any solvents etc. Which volatilise. These films on ageing/storage become more resistant to solvent action or mechanical removal.

Other drying method include Heat polymenzation and infrared curing. Both work in more or less similar manner as described above. Thus in formulating deinking chemicals the various ingradients should be balanced in such a way as to effectively attack and emulsify or remove most of these components. These aspects are described later in the text.

Carbonless Copy Papers

A schematic representation of C C papers is shown in figure 1 and shows the primary components of the top writing paper and the bottom receiving paper.

These two respectively contain the (a) Microcapsuls, (b) binder coating media and the Acid receiving clay or polymers.

However the C C paper respond very well to simple saponification and bleaching treatment as shown in table VI.

A Comparison of Washing & Flotation

The two widely pracised technologies of Deinking processes are based on the operation and processing of the seperated ink particles/carriers in either a deinking Flotation cell or in subsequent washing stages.

The various pros and cons of these systems are discussed herein.

Comparison of De-inking Systems
Washing Vs. Flotation

Washing

Advantages

System has inmherent stability can handle very varying raw material input and general operator malpractice. Low capital cost. Low chemical cost (i. e. cheaper recipes). Can use lower grade waste. Can reduce ash content-or can control ash content. (Most important for tissue).

Excellent physical properties of stock produced.

Disadvantages

Sometimes not highest efficiency (yield). (i.e. 90–95 percent) More complex water circuit. With low consistency washing systems water consumption high.

Flotation

Advantages

Can giver very high yield (i.e. 95 per cent).
Simple water system.
Easily closed system.

Disadvantages

High capital cost. High running cost (Chemicals). No control of ash reduction. Often ash not reduced. Requires more expensive raw material. Very susceptible to operation upset. Requires very careful operation control. Often physical properties of stock produced not too good. The first stage of seperating the ink particles from the films is common to both systems, whereas their subsequent removal takes place through a series of washing and thickening stages in one operation and through flotation and foaming in the other. The latter system requires foaming agents and also collectors which attach the ink to the air bubbles. The process also requires an aeration tank and thus on the whole is more complicated.

Technological Considerations for A Good Deinking Agent

An effective deinking chemical/product is a formulation which provide the different and diverse requirements of the three or four basic principles of deinking. These are :

a) Good emulsification and removal of drying oils and Hydrocarbon bases.

b) Solvent action and/or dispersion of pigment particles and their removal from films.

c) Solvent action and dissolution of varnish films or Acrylic heat set films.

d) Solulization/dispersion of "Stickies" e. g. waxes, bitumen etc.

Considering these aspects the formulation generaly contains

a) Organic solvents which are cheap and effective e. g. toluene, Acetone, Perchlore ethylenes etc. Non-Toxicity is important.

b) A good dispersing or emulsifying agent.

In this class, various detergents which are used for washing powders are included e.g. Common surface active agents such as Alkyl Anyl Sulphonates or the new generation lenear Alkyl Benzenes are also quite effective (LAB).

However in Deinking process it has been established that these agents perform well if their H.L.B. No. (Hydrophilic/Lipohilie Balance Ratio) is high.

HLB No. Range of 15–18 has been found to show very effective ink removal and prevent subsequent redeposition of pigment particles on white papers which is a serious drawback sometimes.

c) Suspending chemicals such as CMC (Carboxy Methyl Cellulose) for holding dirt particles fillers etc. in the suspension. In addition the process of Deinking requires an initial treatment of the waste papers with Approx. 1% NaOH and 0.1–0.5% Sodium Silicate in order to emulsify Oils and waxes etc. Sodium Silicate stabilises the pH of the suspension.

With these essential components it is possible to formulate one or more Reagent which will take care of the basic requirements of the Deinking process. In addition there are mechanical and equipment design aspects of equipment which are equally important for a good deinking process.

Bleaching

All deinking cells incorporate a final bleaching stage using either Sodium Chlorite Na(Clo)2 or H2O2 (Hydrogen Peroxide) in order to obtain a good overall brightness and also bleach coloured pigments.

In case Deinking cells are not used it is necessary to use an alternative bleaching system with Hypochlorite (NaOcl) in the Hydra pulpers or belaching chests.

Although this would increase the overall cost the quality of Deinked waste paper will definitely improve substantially.

Conclusions

1. Thus in conclusion it is strongly felt that more emphasis on increasing waste paper utilization should be given by the Indian Paper Industry.
2. Adequate technological understanding for waste paper treatment should be made available to processors.
3. More economic and effective deinking formulations should be explored and marketed by the Chemical/Auxilliary firms.

Acknowledgements

The authors are thankful to the management of Parkhe Research Institute, for permission to publish this paper and for their continued support and encouragement.

References

1. S C Jain, IPPTA, Presidential Address December 1985 Zonal Meeting New Delhi.
2. Pulp and Paper International (PPI) Oct. 1982 PP 65.
3. Paper August 1980 PP 23.
4. TAPPI, July 1979 PP 25.
5. Paper August 1979 PP 121.
6. Paper January 1978 PP 71.
7. TAPPI, August 1977 PP 114.

TABLE - I

FAO PROJECTIONS FOR SHIFT IN FIBRE USES IN PAPER INDUSTRY

A) GLOBAL TRENDS

(All figures in '000 m.t.)

	Year 1972-74	Year 1990
a) Total paper & paperboard production	145,893	255,820
b) Total Fibre furnish	157,278	272,065
c) waste paper fibre	036,359	73,583
d) Percentage of waste fibre over total furnish	24.7	28.8

B) CONSUMPTION PATTERNS OF WASTE PAPER IN INDIA

Year	Indigenous	Imported	Total
	(All figures in Lakh Tonnes)		
1982	2.0	06	2.6
1983	2.25	1.0	3.25
1984	3.0	1.5	4.5
1985	3.0	2.0	5.0
1990	-	-	10.0

TABLE - II

EXPERIMENTS WITH ORGANIC SOLVENT FORMULATIONS

Paper	Printing	Yield %	Brightness %	Removal	Remarks
Label with varnish overprint (Pringles)	Rotogravure	93	77	Very good	Pink Tinge
Label (Red Gum)	Offset	97	40	Very good	Very little
Label (Winstone Gold)	Rotogravure	91	77	Very good	removed
Coated bleached board (cheese)	Offset	98	77	Very good	Slight Green tinge
Coated book (Thilmany brochure)	Offset	83	84	Very good	Slight purple tinge
Bible paper (Catlogue)	Letterpress	98	69	Very good	Most printing left
Coated magazine(Nati. Geographic)	Letterpress	97	74	Fair	Some printing left
Magazine (U.S. News & World report)	Letterpress	98	62	Poor	Much printing left
News (Kalamazoo Gazetter	Letterpress	99	47	Very poor	Most printing left

TABLE - III

A) TYPES OF INK AS CLASSIFIED BY MAJOR PRINTING PROCESSES

Process	Single Film thickness, UM
Letterpress	4 -- 6
Litho offset	15 -- 3
Gravure	3 -- 12

B)CONSTRUCTION OF ABSORPTION INKS

	Letter Press news	Litho Press news
Pigment, %	9 - 15	10 - 18
Mineral Oil, %	80 - 89	20 - 50
H/C resin, %	--	10 - 30
H/C Pitch, %	2 - 5	2 - 5
Material seal oil, %	--	20 - 30

TABLE - IV

A) HEATSET INK COMPONENTS

Solvents	- Hydrocarbon kerosens fractions - Boiling point range 415-535 (213-279°C) - Typical content 30-40%.
Resins	- Pentaerythritol esters of rosin saturated - hydrocarbon resins Functional hydrocarbon - resins phenolic modified rosin esters - Typical content 30-40%.
Additives	- Gelling or chelating agents - (Aluminum soaps, Al (POH)3) - Alkyd resins - Oil modified Oleoresinous - varnishes waxes, driers, slip agents - Consolvents (alcholds, glycol ethers) - Typical content 5-20%.
Pigments	- 12 - 20%

B) TYPICAL PUBLICATION ROTOGRAVURE INK

Pigment	- 6-10%
Solvents	- Hydrocarbon blends, i.e. - lactol spirits, 60-70%.
Limed-zincated rosin	- 20-30%
Additives (waxes, slip agents)	- 1-4%

TABLE V

A) OXIDATION DRYING SHEETFED INKS

Pigment	- 12-22%
Solvents	- Kerosene fractions. - Boiling point range 470-590°F - (243-310°C 5-20%)
Binders	- Oil-modified alkyds oleoresinous varnishes Rosin esters, phenolic modified rosin esters 55-70%.
Additives	- Driers, waxes co-solvents (alcohol, esters, glycol ethers) 5-15%.

B) CATALYTIC OVERPRINT VARNISH

Solvent	- 40-60% (Lower alcohols, xylene, toluene aliphatics)
Binder	- Hydroxyl terminated polyesters, etherified amino resins.
Catalyst	- P-toluene sulfonic acid.

TABLE VI

A) RELATIONSHIP OF HLB NUMBER TO EMULSIFIER USE

HLB number	Use
4-6	Water in oil emulsifier.
7-9	Watting agent.
8-18	Oil in water emulsifier
13-15	Detergents
15-18	Solubilizing agents.

B) LIST OF SURFACE ACTIVE AGENTS

Manufacturer	Brand Name	HLB
Diamond Shamrock	Hyponic PE- 90	12.9
	Hyponic PE- 100	13.4
	Hyponic PE- 120	14.1
ICI United States Inc.	Span 20	8.6
	Span 60	4.7
	Span 80	4.3
	Tween 20	16.7
	Tween 60	14.9
	Tween 80	15.0
Sandoz Colors & chemicals	Cartan X- 12	14.5
Rohm and Hass	Triton N- 101	13.4
	Triton CF- 10	14.0
	Triton X- 15	3.6
	Triton- 45	10.4
	Triton- 100	13.5
	Triton- 155	12.5
	Triton- 405	17.9

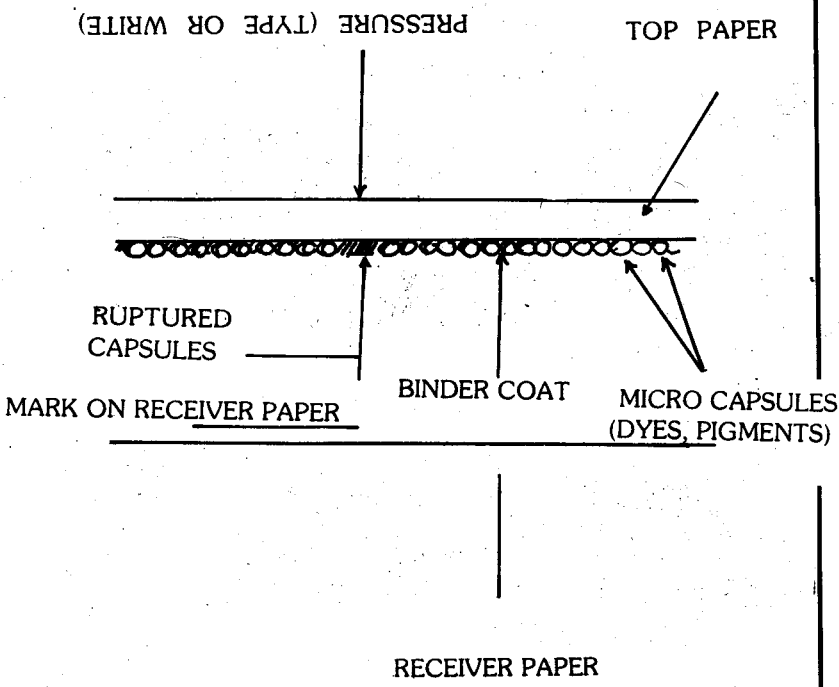

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FIGURE NO. 1