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A Comparison of the Deinkability of Certain Printing Inks

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A COMPARISON OF THE DEINKABILITY OF CERTAIN PRINTING INKS

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ABSTRACT

Printing inks differ in their composition and in their ability to be removed from paper in the deinking process. It was the purpose of this research work to make a comparison of this deinkability, for common printing inks.

In this experimentation, five inks were compared. These were a linseed oil base ink, a mineral oil base ink, a moisture set ink, a alkyd base ink, and a rubber base ink. Deinking was done using a standard deinking formula and varying only the concentration of the deinking agent.

The results show a marked difference in concentrations of deinking agent necessary for deinking different inks. Some of the inks deinked at low concentrations of deinking agent, while others required higher concentrations. The rubber base ink could not be deinked with the method used in this experimentation.

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LITERATURE SURVEY

INTRODUCTION

Waste paper is an important raw material for the paper industry. In areas which do not have a ready supply of virgin pulp but which are near large population centers, the utilization of waste paper as a substitute for virgin pulp presents many advantages. Among these are:

1. Lower cost of waste paper over virgin pulp.
2. A decrease in bulk, desirable in book, magazine and writing papers.
3. An increase in opacity.
4. Better formation because of the relatively low freeness produced, resulting in a well-closed, dense, fairly snappy sheet.
5. Higher retention of size and filler.
6. Lower cost of the deinking installation as compared to a pulp mill.

Some disadvantages include: (1) poorer control of the quality of the resulting paper than with virgin pulp due to the many variations in the wastepaper used, (2) an increased difficulty in obtaining suitable waste paper because of the increased use of synthetic fibers and of nonfibrous materials in coatings and adhesives which present difficulties in the deinking process and (3) stream pollution caused by deinking mill effluents which often results in the mill building expensive treating plants.

A large part of waste paper has been printed necessitating an operation to loosen and separate the printing ink from the wood fibers in the paper. This process is called deinking. It consists of defibering the waste paper by mechanical action with water, heat and suitable chemicals, usually alkali to loosen the ink from the paper by saponifying, dissolving and emulsifying the ink vehicle. The pigment set free is removed by washing. Although theoretically the deinking reaction is quite simple, the process is complicated by the grades of wastepaper used, the type of printing ink involved and the end use of the recovered pulp.

PRINTING INKS

A high per cent of waste paper has been printed by a great variety of printing inks of every name, brand, and description. Fortunately, these many different inks can be "boiled down" to several basic formulae or types of ink, at least from a deinking point of view. The purpose of this thesis was to make a comparison of these inks for their relative ability to be deinked (deinkability).

THE INK FORMULA

Basically a printing ink consists of a pigment suspended in a vehicle. The pigment is a finely divided material which gives body and color to the ink. Carbon black is usually used in black inks while colored organic coal tar derivatives or inorganic colors such as natural earths or precipitated pigments are used in colored inks. The pigment is resistant to the action of deinking alkali. The vehicle usually consists of a vegetable or mineral oil in combina-

tion with dryers, thinners, resins and special compounds. Linseed oil (a vegetable oil) makes up about 75 per cent of all oils used in printing inks.

DRYING

The composition of the vehicle depends on the type of ink desired and how it is to be used. The main concern is the type of drying which will take place. The types of drying usually encountered in printing inks are:[1]

1. Oxidation of the oil vehicle by air
2. Polymerization
3. Precipitation of solids from a solution
4. Evaporation of a solvent
5. Penetration and absorption
6. Solidification

CLASSIFICATION OF INKS

From a deinking standpoint there are three general classifications of inks:

1. Those with an alkali-saponifiable vehicle
2. Those with an alkali-nonsaponifiable vehicle.
3. Special inks very resistant to deinking, made from synthetic resins and organic solvents.

Inks with alkali-saponifiable vehicles are those inks which dry by partial oxidation, polymerization and condensation. Most vegetable oil base inks fall into this class. These inks are readily saponified by alkali. Mineral oil base inks make up most of the second classification. These inks dry by absorption of the vehicle into the paper. However, completely oxidized oil base inks are also

alkali-nonsaponifiable and fall into this group. This up and the third group of special inks are not completely saponified by alkali and need to be deinked by special methods.

SPECIAL INKS

Certain special inks are: (1) heat-set inks consisting of a solid in a volatile solvent which is driven off by the application of high temperatures leaving a hard film, (2) cold-set inks consisting of a thermoplastic resin which is made liquid by heating and which solidifies immediately on contacting the comparatively cold paper, (3) aniline base inks made from aniline dyes with alcohol as a solvent and shellac or tannic acid as a binder (adhesive) and, (4) moisture set inks which have a resinous binder dissolved in glycol solution; the binder being precipitated on the sheet by excess moisture.

HISTORY OF DEINKING

Deinking was first known to be carried out by Mattias Koops in England in 1800 using a solution of pearl ash (potassium carbonate) as a solvent of the ink vehicle and as a detergent.[2] Although considerable paper was made and sold, the company went bankrupt in 3 years. In the United States the first deinking process was used by Henry E. Rogers in 1849.[2]

EARLY METHODS OF DEINKING

Some of the earlier methods of deinking, some of which are still in operation were:

1. Cooking in Covered Hollander Beaters.

In this process an insulated iron tub beater with a capacity from

1200 to 1500 lb., was used. About 10 per cent soda ash, based on the weight of the paper treated, was added with enough water to give a stock consistency of 6 per cent. After heating with steam to a temperature of 190-210 F, the stock was circulated and fiberized by the beater roll for 1½ hours with the steam on. After two to three hours, the batch was discharged into a storage tank for washing. Operating costs for this system were high because of the small batches.

2. Open Tank Cookers.

This process included several cylindrical steel tanks about 10 feet in diameter and 10 feet high. Each had a perforated steel bottom with an 8-inch diameter pipe rivoted to it vertically. By this means the load could be lifted out. The steam which was turned on below the false bottom forced the alkaline liquor up through the central pipe against a baffle, resulting in liquor being sprayed over the paper stock. Circulation could be improved with a centrifugal pump. A consistency of 5 to 6 per cent gave best results. After several hours of cooking the load was transferred to another, and the same process repeated. The liquid drained off, was strengthened and returned to the system. A cook required from 6 to 15 hours. Consumption of soda ash was 6.7 per cent.

3. Rotary Pressure Cookers.

This cooker was a horizontal cylinder about 8 feet in diameter by 24 feet long, handling 5 to 7 tons of paper. Steam was injected as the cooker rotated from three to six hours. Percentage of alkali varied from 3 to 10 per cent. Globe rotary boilers were also used in the same capacity. This system was regarded as a definite

improvement over the two previously mentioned but has become largely obsolete.

4. Winestock Process.

In 1910 the Winestock Process was patented. In this process the deinking was largely mechanical. Defibering action was caused by thrashing propellors in a cylindrical tank of special arrangements. This machine also maintained perfect circulation until all the stock was defibered. A cook of about 900 lb. of paper, took about one hour at 160 to 180F and 5 per cent soda ash.

MODERN METHODS

Modern methods of deinking are carried out in the following steps:

1. Sorting to remove objectionable paper and trash
2. Pulping and Cooking to loosen ink and set free the pigment
3. Washing out the loosened ink pigment

   Riffling and Screening
5. Bleaching
6. Rewashing for removal of chemical residues
7. Thickening for use or storage

There are no standard conditions for cooking and disintegration (deinking) and practices differ widely in different mills. However, in principle, they are all alike in that the wastepaper must be mechanically defiberized in water. Chemicals are added at some point in the process and heat generally is needed to hasten the deinking action.

general there are three different methods:[3] (1) low den gration followed by cooking in a separate cooker, (2) disintegration in a beater or pulper followed by cooking in the same pulper and (3) cooking in a cooker without prior disintegration. Either low (4 to 10 per cent) density or high (20 to 35 per cent) density disintegration is used in the last two methods.

In the first methods, the stock is broken up in a breaker beater or pulper at a consistency of four to nine per cent. After pulping, the stock is cooked in a stationary circulating type cooker or a rotary cooker at 160 to 210 F from 1 to 5 hours. Experimentation has shown that the initial disintegration causes 77 per cent of the total deinking and defibering, and the following cook produces 21 per cent.[4] The above method is used by most mills.

The second consists of pulping and cooking the stock in the same pulper which may be a larger beater, hydropulper or a tank and pumping system. Pulping may be either low or high density with variations from 7 to 25 per cent. High consistency pulping speeds up defibering, reduces the amounts of chemicals needed, and produces a pulp of higher freeness than low consistency pulping. Cooking time is from 2 to 5 hours at a temperature range of 140 to 180 F.

In the third method, cooking and defibering are done simultaneously in globe rotary boilers at either high or low density. The dry paper along with the chemicals and hot water, is fed directly into the boiler. Cooking temperatures range from 170 to 200 F and the cooking time varies from 3 to 8 hours.

DEINKING ACTION

According to James Strachen,[5] the following action takes place in the deinking process:

1. Neutralization of alum in the paper followed by rapid percolation of the cellulose by the alkaline liquor.
2. Saponification of the natural resins and sizing in and around the cellulose fibers and to a limited extent, the dried oily ink vehicle, followed by a loosening of the adherent films of the latter.
3. Complete loosening of dried ink by the friction of the fibers against each other.

Alkalies are used in deinking, for two reasons: (1) to remove rosin sizing from the paper and (2) to saponify the ink vehicle and release the ink pigment. For drying inks, vegetable oil-base inks which are only slightly oxidized, saponification takes place readily with alkali. However, nondrying mineral oil-base inks, completely oxidized oil base inks and inks having a synthetic resin base cannot be completely saponified by alkali. Special methods are used to deink papers containing these inks.

One writer claims that oxidation and reduction play an important part in deinking, especially in breaking down resistant inks. He says that ink is an oxidized material and the alkaline cooking liquor acts as a reducing agent. The more highly oxidized an ink

As a result, one reducing catalyst

and alkali mixture causing rapid disintegration."[1]

The alkalies used in deinking do not have the ability to sufficiently emulsify the ink particles. Therefore, a detergent such as soap is used to wet and emulsify the particles of ink pigment. The detergent sets up a repelling action between the fibers and the particles so that they are easily removed by washing.

After the pigment has been released, dispersing agents are sometimes used to prevent agglomeration of the pigment particles and absorptive agents to prevent the pigment being deposited back on the surface of the now absorptive fiber.

CHEMICALS USED

The two alkalies most generally used are sodium carbonate and sodium hydroxide. At present, more sodium carbonate is used, but the tendency is toward sodium hydroxide because of the need for stronger treatment for modern printing inks. Caustic soda alone, gives harsher treatment and faster action resulting in greater fiber loss and degradation and a yellowish colored pulp. Comparatively soda ash has a slow rate of action but results in less oxidation of the pulp, giving less fiber loss and a whiter pulp. Using the two together seems to be the best deinking formula giving a satisfactory rate of cook with minimum fiber loss. About three to eight per cent of sodium carbonate or 2 to 4 per cent of sodium hydroxide is sufficient for most papers. Used together, 2½ per cent sodium carbonate and ½ per cent sodium hydroxide works very well.[2]

Other alkalis include sodium silicate, sodium phosphate and sodium peroxide. Silicate has a higher degree of surface activity than either sodium hydroxide or sodium carbonate and produces a whiter, brighter pulp than either. Peroxides especially in combination with silicate are very effective and result in better fiber separation and often higher brightness than with the alkali alone.[3] Peroxides are also of considerable interest for deinking groundwood.

Wetting agents and detergents include:[6] (1) oleic acid, (2) Gardinol, (3) Du W. A. and E) silic of soda, (5) Dupont MP-202 detergent and emulsifying agent (6) Tergitol and (7) D-1 Lestoil. In deinking, ordinary rosin sized paper, the reaction of the alkali with the size forms rosin soap which acts as a detergent. With unsized papers, no soap is formed and special detergents may be necessary. Soaps and detergents are especially helpful for papers which are hard to deink.

SPECIAL PROBLEMS

In the progress of deinking, certain problems besides those of ink removal, have developed causing a great deal of trouble to deinking mills. Although the waste paper has been sorted and graded by the waste paper dealer and usually resorted at the mill, many times objectionable materials find their way into the disintegrators and cookers. The effect of a small amount of this material is often disastrous, resulting in the ruin of tons of pulp.

Calcium carbonate filled papers are troublesome. This filler has an affinity for ink and causes difficulty by forming insoluble

compounds with the ink. Wet strength papers have a high resistance to fiber separation. Special methods, including high temperature and low pH, are necessary for deinking such papers. Glassine, parchment, waxed, resin-impregnated, and resin-coated papers cannot be defibered by ordinary deinking methods. The spray of flour and water or wax, used by printers to prevent offset; lacquers and varnishes for high gloss; and coatings using insolubilized casein as a binder, also present difficulties in deinking.

Groundwood is another deleterious material. Machine coated papers contain up to 30 per cent groundwood. Such papers are difficult to deink and turn brown during deinking, colored specks in the final pulp. Now, however, groundwood can deinked feasibly by using sodium peroxide.

EXPERIMENTAL PROCEDURE

In my experimentation, samples of an uncoated paper were printed with each of the different inks to be tested. Then each sample was deinked with a standard deinking formula, varying only the alkali concentration.

Five different inks were obtained at the Kelly Ink Company. The inks selected were those which were considered to be representative of the main or basic types of printing ink used. The inks were: (1) a rubber base ink; (2) book black, a linseed oil base ink; (3) news ink, a mineral oil base ink; (4) steam set blue, a moisture set ink and, (5) non-scratch half tone, an alkyd base ink.

The paper which was selected was 50 lb. Custom offset, an uncoated paper. It was decided to use an uncoated paper so as to work with the basic fiber to ink bonding instead of becoming involved with the deinking of coated or sized papers which presents new aspects to the problem of deinking. This paper was used as the standard throughout experimentation.

Before any deinking could be done, it was first necessary to apply the ink on the paper in some manner. Preliminary experimentation was carried out using different methods of applying the ink to the paper.

First a Meyer draw rod was tried. This possibility was quickly ruled out. Even with the highest numbered rod, the ink layer applied was much too thick and hard to control, being dependent to some extent on the pressure applied by the person drawing the rod.

Another method which was tried was that of inking a smooth plate with a rubber hand roller, and then pressing the sheet against the

plate with a similar roller. It was found that the amount of ink couldn't be controlled nor did the sheet make good contact with the plate unless a thick layer of ink was used.

A Vandercook proof press was another possibility. At first this was thought to be satisfactory. The amount of ink put on the rollers could be measured with an inkometer. However, after several preliminary cooks with different inks, there was found to be very little difference in their deinkability. The conclusion was reached that it isn't the lightly printed papers which cause trouble in deinking but the heavy blacks and solid printed papers. Printing a heavier coating of ink could not be done very effectively with the Vandercook on this paper because the paper was uncoated and had a rough surface.

The method decided on was that of using a laboratory knife coater to apply the ink. This coater put on a satisfactory coating of ink which could be controlled fairly accurately.

All inked paper was dried by the atmosphere. Since under actual conditions waste paper contains from ½ to 1 per cent ink, the printed paper containing 30 per cent ink, was mixed with blank paper giving a final mixture of 1 per cent ink. This mixture was then deinked.

Deinking was done in 1 liter, stainless steel beakers using an Atlas drill press with a 2 inch agitator, at 2133 1/3 r.p.m. for agitation. The action obtained with such a set-up is very similar to that of a hydrapulper. Two gram samples were taken at half hour intervals and made into handsheets on the British Sheet Mold. After drying, the handsheets were inspected visually and tested for brightness on the Photovolt brightness tester.

Book black ink, a linseed oil base ink, was used as a basis of comparison. The reason for this, was that this ink represents the most common class of inks and presents no problem in deinking. With this ink, a standard deinking formula was determined. The formula was 5 per cent sodium hydroxide; 1 per cent detergent (D-1 Lestoil); 5 per cent Bentonite (a clay used for absorbing the freed pigment) based on the weight of air dry paper; 5 per cent consistency and a temperature of 185 F.

With this formula it was possible to deink book black effectively in one half hour. The other inks were deinked using the same formula, changing only the concentration of the sodium hydroxide until satisfactory deinking occurred.

RESULTS

The handsheets made from the deinked stock were tested for brightness with the Photovolt brightness tester. The sheets were also visually inspected for undispersed ink particles.

Of the five inks tested, book black, a linseed oil base ink, was the easiest to deink. With this ink it was possible to deink the printed paper with 5 per cent sodium hydroxide in one-half hour giving a brightness of 63 in comparison to the original brightness of 70 for the standard paper. In this time, all ink particles visible to the naked eye were broken up and dispersed.

Steamset blue, a moisture set ink, was also relatively simple to deink. All ink particles were broken up and dispersed in one-half hour with 5 per cent sodium hydroxide. However, the resulting handsheets had a brightness of only 55. Increasing deinking time to 1½ hours resulted in a brightness increase to 57.5.

The alkyd base ink gave more trouble in deinking than the previous two inks. At a 5 per cent concentration of sodium hydroxide, this ink was not broken up effectively. The handsheets were spotted with unbroken ink particles. Increasing the concentration of sodium hydroxide to 7 per cent broke up and dispersed the ink particles and gave a brightness of 57 in one-half hour.

The news ink, a mineral oil base ink, was not completely broken up at 8 per cent in one-half hour. At this point a few spots of unbroken ink particles remained. In one hour deinking was almost complete and the brightness of the handsheet was 54. After 1½ hours of deinking the brightness reached 58.

The rubber base ink was the most troublesome of all the inks tested. This ink could not be deinked by the methods used. Balls of ink as large as 2 mm. in diameter formed at a 5 per cent sodium hydroxide concentration. Increasing the sodium hydroxide concentration had some effect on the ink balls in that this decreased their size to some extent. However, a concentration of 12 per cent sodium hydroxide failed to break up or reduce the ink balls completely. Handsheets made with the resulting stock were very conspicuously spotty.

SUMMARY AND CONCLUSIONS

This experimentation has served to confirm opinions that printing inks differ in their resistance to deinking. Some deink quickly and easily and at low concentration of sodium hydroxide while others are difficult if not impossible to deink. The results of this experimentation seems to give an indication of the relative deinkability or ease of deinking, of the five classes of inks tested.

Book black representing that class of inks with linseed oil as a vehicle, is comparatively easy to deink and presents no difficulty in deinking. Steamset blue representing the moisture set inks, was also easy to deink although it was not possible to reach such a high degree of brightness as with book black. These two inks deinked at 5 per cent sodium hydroxide in one-half hour. The alkyd base ink representing that class of inks with alkyd resins as an ink vehicle gave a little more trouble in deinking [illegible] d [illegible] t 7 per cent, in one-half hour. The news ink representing that class of ink with mineral oil vehicles, deinked at 8 per cent sodium hydroxide in $1\frac{1}{2}$ hours. The rubber base ink representing that class of inks with a rubber latex vehicle gave the most trouble of [illegible] nks tested. At a concentration of 12 per cent sodium hydroxide, deinking was still far from complete.

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