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Deinking of Coated Magazine Papers: Experiments with Some Enzymes

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DEINKING OF COATED MAGAZINE PAPERS
Experiments with Some Enzymes

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Literature Survey

A. Introduction

At the present time fairly harsh procedures are used to deink magazine waste paper. The paper must be cooked in the presence of strong chemicals such as sodium hydroxide at elevated temperature and in some cases this is even carried out under pressure. This results in the removal of ink but the fibers are considerably darkened due to this procedure (1,2). It was the object of this survey to explore the literature to see if there is any information on a relatively mild method involving enzymes, which due to the absence of harsh chemicals and high temperatures would possibly result in a deinked fiber with a minimum of discoloration and reduced shrinkage in yield.

B. Definition of Terms Involved

1. Deinking - The Dictionary of Paper defines deinking as follows (3). "The operation of reducing printed papers to pulp and removing the ink therefrom by mechanical or chemical means." The paper is disintegrated mechanically and then treated with caustic and/or soda ash and dispersing agents. This allows the ink along with other extraneous materials to be removed when the treated stock is washed (3).
2. Magazine Papers - Magazine papers are papers used for periodicals. There are many grades and finishes available both coated and uncoated (4). For example, the inner pages of Life and Look magazines consist of a 28 lb. (25 x 38-500) body stock coated with 5 lb. (felt side) and 7 lb. (wire side) coating solids resulting in a 40 lb. (25x38-500) finished sheet (5).

The body stock of mass produced magazine paper may consist in many cases of mixtures of coniferous groundwood and coniferous chemical pulp, of coniferous groundwood, deciduous semichemical pulp and coniferous chemical pulp or of other mixtures which are usually high in lignin content (6).

3. Coated Papers - Coated papers are a grade of papers where in most cases the surface is covered with a coating of pigment and adhesive (7). The pigments consist of clay, titanium dioxide, calcium carbonate and other water insoluble substances. The adhesives are made up of proteins, starch, casein or synthetics in the form of latex. The adhesive binds the pigment particles to the fiber as well as to other pigment particles. In the case of magazine papers, utmost economy is necessary in formulating the coating. Thus, most magazines are coated with pigment bound by the most economical adhesive, namely starch (6).

C. Enzymes

1. Definitions - Enzymes are described by Schwalbe (8) as brocatalysts made up of an organic substance having the ability to accelerate reactions. These catalysts are produced by living cells and do not only accelerate reactions but can select one reaction over another (9).

It is highly probable that all enzymes are protein in composition. This is believed since their general properties such as stability and their behavior toward acid, alkali and heat all indicate proteinaceous nature. It is also believed that they belong to different types of proteins with the molecular weights varying from fifteen thousand to two hundred thousand. Although their extraordinary catalytic properties mark them as different from ordinary proteins, their structure does not appear unusual. Enzymes may also undergo denaturation like other proteins and when this happens the enzyme is inactive (9).

An inhibitor causes partial depression of enzyme activity whereas an inactivator partially or totally destroys the enzyme. Protein reagents, heat, acid, alkali, supersonic vibration and high hydrostatic pressures destroy enzyme activity. It may also be noted that two enzymes do not react in the same manner under the same circumstances (9). The substance which undergoes the accelerated chemical change is called the substrate. Enzymes are named after their substrate by adding the suffix "-ase". Coenzymes are organic molecules which attach themselves to enzymes to make them active. Other substances that increase activity are called activators (9).

2. Formation and Action of Enzymes - It has not been determined how an enzyme is produced but it is known to be not self-duplicating. Therefore, very little is known of enzyme formation.

It has been shown that greater concentrations of substrate give a faster reaction. This substrate has a specific affinity for the enzyme. Measurements of this affinity show the efficiency of the enzyme. However, it is also found that the end products can also combine with enzyme to produce a "competitive inhibition" which slows down the reaction. Other substances can form with enzymes to inhibit reaction and even keep the enzyme - substrate complex from forming. In measuring enzyme activity it may be assumed that the amount of change over a given interval is proportional to the amount of catalyst. However, this is an oversimplification and research is needed to define limits (9).

3. Enzyme as Catalysts - The ability of enzymes to select one reaction over another as previously mentioned is known as specificity. Specificity may be subdivided into four groups; absolute, in which the enzyme works on only one substrate; group, where the enzyme works on a series of substances but only if certain groups are present in the molecular chain of the substrate; reaction, which is the lowest degree of specificity since the reaction is dependent only upon the type of linkage; steriochemical, where the enzyme can actually differentiate between mirror images (13).

It is uncertain as to how enzymes work. The following is a commonly held belief on this topic. It can be imagined that the surface of an enzyme is distorted and when combined with a substrate, the substrate becomes distorted causing bonds to break at a faster rate than normally. Here is demonstrated the fact that the enzyme is only a catalyst since the reaction would occur anyway only at a slower rate (9). This rate at which the reaction takes place varies with the enzyme used according to Casey (10). Enzymes can either synthesize, as in the case of phosphorylases, or hydrolize as in the case of amylases (9).

4. Amylolytic and Proteolytic Enzymes - All enzymes may be classed into one of four groups: enzymes of hydrolysis, enzymes of oxidation, enzymes of transfer and mutases. Those that degrade glycosidic molecules and proteins are grouped under enzymes of hydrolysis. The general reaction is the adding of water to bonds to cause a separation.

Amylolytic enzymes or carbohydrases hydrolyze the glycosidic bond. This group may be subdivided into alpha and beta amylases. Alpha amylases split starches into dextrins and then continue to form maltose and traces of glucose. This results in the destruction of the branched chain structure which is known as amylopectin. It is important to note that almost complete degradation can be obtained. Beta amylase only partially degrades starch but does not affect the branching points. It is found that when the branching points are attacked by alpha amylase, the straight chains formed are then readily attached by the beta amylase. Thus the two enzymes together hydrolyze starch more rapidly than either alone (9).

Proteolytic enzymes catalyze hydrolysis of protein. These may be divided into two groups: proteinases and peptidases. In the case of the proteinases, the proteins are hydrolyzed to peptides and partially to amino acids. Native protein is split very slowly whereas degradation products of protein are split rapidly. The peptidases split peptides to amino acids.

5. <u>General Conditions for Enzyme Use</u> - Many variables effect the action of enzymes. Some ions such as zinc, nickle, ferric chromium and aluminum are toxic while others such as copper, silver and mecuric ions are extremely toxic to enzyme action. However, other ions, particularly calcium as well as the alkali earth metals, stabilize the enzyme activity (8). This stabilizing effect allows the enzyme to function at higher temperatures (11). In cases where the toxic ions are present, an addition of a calcium phytate compound forms non-ionized complexes with these heavy metal ions (8). Although these ions are present in water, their minute concentration makes

them of no importance to enzyme activity except in cases of extremely hard water (11).

The pH of the mixture is of extreme importance. Although the preferred pH varies with the enzyme an acceptable pH range for enzyme conversion of starches is from six to eight (12). This range may be extended to nearly nine if the conversion is carried out in the presence of urea. This will in turn reduce the enzyme requirement but will also reduce the degree of degradation (11). For raising the pH of the solution, calcium carbonate is usually used (8). The pH requirements for protein conversion may run as low as one (13). However, some commercial protein enzymes are now produced that convert at a pH of about seven (14).

The presence of pigments used in papermaking or coating of paper have a marked effect on enzyme activity. The pigment particles absorb enzyme, thereby reducing the amount of available enzyme. The absorbtive power may be reduced by means of one percent sodium silicate with respect to the pigment (8).

D. Deinking with Enzyme

The literature search for methods for deinking with enzymes revealed no pertinent information. Therefore, it was decided to carry out some experimental work in this seemingly new area.

Experimental Design

In designing the experiments to be carried out, it was planned to use amylolytic and proteolytic enzymes for digestion of two types of natural adhesives contained in coated paper. The inner pages of a well known starch-clay coated magazine for amylolytic and printed casein coated paper for proteolytic conversion was to be obtained.

Two approaches were to be attempted; first, to soak the paper in tap water and then allow the enzyme to digest the adhesive before disintegration; second, to disintegrate the paper and then allow the enzyme to act. It was expected that the digestion would release the printing ink from the fibers and therefore, this ink could be removed by either flotation or conventional washing on inclined screen washers.

From the resultant stock slurry, hand sheets were to be formed to run such tests as reflectivity measured in percent brightness and inspection for cleanliness.

Experimental Work

1. Materials Used

a. Enzymes - Two types of enzymes were used in these experiments. The amylolytic enzyme, Amylic, was used to attempt to liquify the adhesive in the printed paper using a starch adhesive and the proteolytic enzyme, Serizyme, in the printed paper with a casein adhesive.

b. Detergent - A commercial detergent, Triton X-100, was used to disperse the pigment particles during disintegration.

2. Equipment Used

a. Drill Press Agitator - This instrument was used to disintegrate the paper in the deinking procedures. It runs at a speed of two thousand two hundred revolutions per minute using a long rod with a circular impeller on the end to perform the disintegration. The impeller was formed from a circular piece of metal that has had four slits, evenly spaced, cut from the edge to within about one inch of the center. The right hand edge of the slit has been bent upward and the drill press turns in such a way so that the stock is forced down toward the bottom of the container.

b. Side-Hill Washer - The side-hill washer is composed of a screen, tilted at forty-two degrees, mounted on a portable box. The pulp at about one percent consistency is poured over the top of the screen and then water from a hose is used to wash off the collected fiber. Screens of both sixty and forty mesh were used in these experiments. The washer was made by the Kalamazoo Tank and Tile Company.

3. Methods Used for the Deinking Process

One basic method of deinking was used for the body of this experimental work. All the printed paper used was cut into one inch squares and placed into a three-liter metal beaker. Water at one-hundred seventy degrees Fahrenheit for the amylolytic enzyme and one-hundred thirty degrees Fahrenheit for the proteolytic enzyme was added to bring the consistency to four percent. Enzyme was then added in the instances that required its use and in all cases a time period at constant temperature varying from three to thirty minutes followed. The temperature was maintained in a water bath. After the soaking period a dispersant and, in experiments requiring such, sodium hydroxide was added and the disintegration was started. This disintegration varied between five and thirty minutes. The stock was then poured over a side-hill washer six times at about one percent consistency. The cleaned pulp was dewatered in a buchner funnel and set aside to be compared with other experiments.

4. Data

Table #1 - Deinking of Printed Waste Paper with Starch Adhesive

#9 - NaOH	#10 - Control	#11 - Enzyme	#12 - Enzyme NaOH
clean but darkened by NaOH	Slightly bluish	Slightly bluish	Clean but darkened by NaOH

Time cycle:

1. Thirty minute reaction period at 170° F. (#11, #12 - Add enzyme at start)

2. Thirty minute disintegration at 2200 rpm. (#9, #12 - Add NaOH at start)

3. Wash on side-hill washer.

Table #2 - Deinking of Printed Waste Paper with Starch Adhesive

#13 - NaOH, Enz.	#14 - NaOH	#15 - Enzyme	#16 - Control
57% brightness clean but slightly darkened	57-58% brightness about the same as #13	59-60% brightness Very slightly bluish	59-60% brightness Very slightly bluish

Time cycle:

1. Fifteen minute reaction period at 170° F. (#13, #15 - Add enzyme at start)

2. Fifteen minute disintegration at 2200 rpm. (#13, #14 - NaOH added at start)

3. Wash on side-hill washer.

Table #3 - Deinking of Printed Waste Paper with Starch Adhesive

#17 - NaOH + Enzyme	#18 - NaOH	#19 - Control
61% brightness very clean	61% brightness very clean	62% brightness very clean

Time cycle:

1. Three minute reaction period at 170° F. (#17 - Add enzyme at start)
2. Five minute disintegration at 2200 rpm.
3. Five minute disintegration at 2200 rpm. (#17, #18 - Add NaOH at start)
4. Wash on side-hill washer.

Table #4 - Deinking of Printed Waste Paper with Protein Adhesive

#20 - Control	#21 - NaOH + Enzyme
Large flecks of pigment and ink remained	Same as # 20

Time cycle:

(See Table #3) Temperature = 130° F.

Table #5 - Deinking of Printed Waste Paper with Protein Adhesive

#22 - Enzyme + NaOH	#23 - NaOH
Flecks of pigment and ink still present	Same as #22

Time cycle:

1. Twenty minute reaction period at 130° F. (#22 - Enzyme added at start)

2. Twenty minute disintegration at 2200 rpm. (Add NaOH at start)

3. Wash on side-hill washer.

5. Discussion of Results

Table # 1 shows a comparison of four experiments using the same procedure for deinking but carried out with different chemicals. The only chemical involved in experiment number nine was caustic and this was added immediately before the disintegration step. The result was a clean pulp slightly darkened by the action of the caustic which was at a concentration of four percent on the fiber. Experiment seven was a control and yielded a pulp that had a bluish cast. This tended to indicate that the deinking was not complete. Number eleven employed enzyme as its only chemical and its use started at the beginning of the reaction period. The deinked pulp closely resembled the control. Number twelve was performed with enzyme and caustic in the same concentrations as used previously. The resultant washed fiber was clean but darkened somewhat due to the caustic. To obtain a more useful comparison it became necessary to reduce the time periods.

Table # 2 gives a comparison of experiments done in the same manner as previously shown but with reductions in time of reaction and disintegration. Since no significant visual difference was observed between these experiments and those already discussed it was decided to change the time periods to an extreme minimum.

Table # 3 gives a comparison of deinking procedures all having the same cycle but with time periods varying markedly from the before mentioned experiments. Here only a three minute reaction was allowed before disintegration. The disintegration was divided into two parts, a five minute cycle without the addition of caustic followed by a five minute period with caustic added at the start of the final five minutes. Experiment number seventeen employing enzyme and caustic gave a clean pulp with a high brightness. Number eighteen, where only caustic was used, resulted in a very clean pulp with a brightness of about 61%. The control gave even a higher brightness and was visually as clean, if not cleaner, than pulps obtained from any previous deinking procedures. It was not believed necessary to perform further experiments with printed waste paper using a starch adhesive and for this reason attention was turned to printed waste paper containing casein as its adhesive.

Table # 4 followed the exact cycle as mentioned in table three except a proteolytic enzyme was used since paper with a protein adhesive was to be deinked. Both the control and experiment number twenty-one incorporated caustic and enzyme for deinking ingredients. Both washed pulps still contained large particles of pigment with ink still on the particles. Therefore, it was decided to lengthen the time cycle and perform further experimentation.

Table # 5 shows the final results obtained in the laboratory. When the time cycles were lengthened equally poor deinked pulps were obtained even though an enzyme was used in the first experiment shown in the table. It was felt that further experimental work would be of no importance and therefore the laboratory work was terminated at this point.

a. Conclusions: It was shown in the first part of the laboratory work that enzymes had no value in a deinking process where starch was used as the adhesive in a printed coated waste paper since water alone could be used to obtain the desired results. In the second part it was shown that enzymes had no value in the deinking of a printed coated waste paper employing protein as its adhesive since an enzyme used with caustic gave no better deinking than the use of caustic alone.

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