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The Effect of Pigments in the Flotation De-Inking of Newsprint

Harold M. Cody
Western Michigan University

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Harold M. Cody

Western Michigan University
Kalamazoo, Michigan

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ABSTRACT

This study was performed to determine the effect of the addition of pigments in the flotation de-inking of newsprint. It has been proposed that pigments aid in the flotation and removal of ink. Two pigments were investigated: talc and diatomaceous earth.

The addition of talc caused the brightness of the sheets to drop because the talc became heavily concentrated with ink. The addition of diatomaceous earth to the cell had no effect upon the flotation and removal of the ink. Therefore the addition of pigments to improve ink flotation and removal cannot be justified.

INTRODUCTION

The de-inking of wastepaper is used on a wide variety of wastepaper grades, to produce a wide assortment of end products. There are basically two types of de-inking systems available today to de-ink wastepaper; washing and flotation.

Flotation de-inking is used extensively worldwide on a variety of grades. There are approximately 110 flotation de-inking systems now operating or on order worldwide, with over 25% started up or on order since 1977. (1) Another 20-30 systems are estimated to be in the planning stage or in the process of being ordered.

The worldwide capacity for flotation de-inking is estimated at around 2.38 million air-dry metric tons. (1) Almost half of this is in Europe, with much of the rest in Japan. The actual growth rate in flotation de-inking is difficult to determine precisely since a significant amount of expansion has been through extension of existing systems and the net incremental increase is not always known. However, it is safe to say that from 1975 to 1978 flotation de-inking capacity in Europe has doubled and has increased by around 50% in Japan. Worldwide, capacity has increased about 70% compared to the end-1975 level.

In North America, flotation de-inking has found only limited application, and the majority of the systems (43 out of 49) utilize conventional washing de-inking. It was felt for many years that flotation de-inking was incapable of producing pulp of acceptable quality. Also, a few years ago, a higher dirt

count was acceptable in Europe than in North America. In addition the low water consumption and minimal effluent problems have made flotation de-inking more attractive for use in other areas of the world. As a result there are currently only six flotation de-inking installations in North America. (2)

Recent advances in flotation de-inking technology and process control (such as those used by Georgia-Pacific in Kalamazoo, Michigan, and Boise Cascade in Vancouver, Washington) are showing this is no longer true and growth in flotation usage in North America can be anticipated. De-inked fiber is an excellent way for mills to increase their pulp supply incrementally without large capital expenditures for pulp mill equipment.

Almost one third of all flotation de-inking systems now in operation or on order supply fiber for newsprint production. If this were measured on a tonnage basis, newsprint production would account for almost two-thirds of the total flotation de-inked fiber. While this is likely to remain this way for some time, flotation is being applied today more extensively to other paper grades, and process improvements will undoubtably continue this trend.

In North America there is one large company that produces newsprint from 100% old news, but they utilize conventional washing de-inking.

Since there is not a single flotation unit in North America de-inking any large quantity of newsprint, the purpose of this study is to investigate this subject.

HISTORY AND DEVELOPEMENT OF FLOTATION

The de-inking of wastepaper is hardly a new process. The first attempt to reuse paper dates back to 1695 and the efforts of George Balthaser Illy from Denmark. (3) Conventional washing de-inking methods have been in use since paper was first de-inked around 1730. The first patent in de-inking was granted to Mathias Koops in 1800 by the British patent office. (3) The earliest patent which may be considered as relating to the flotation process was issued to William Haynes, who in 1860 recognized the difference in wettability of various minerals by oil and water.(4) Since that time flotation has passed through three principal stages of developement: 1) bulk oil flotation 2) skin flotation and 3) froth flotation. The first two methods are now obsolete and have been replaced by the third upon discovery that air bubbles become attached only to hydrocarbon mineral surfaces. (7)

Flotation was initially used mainly in the ore and mineral industry to concentrate the various ores from the other materials present.

De-inking on a large scale really began during the twentieth century. In the mid-thirties, Kowalewski reported on the removal of printing ink by flotation, and described the construction of a flotation cell for this prupose. (5) (6) During the early years, it was just what the name implies; a method of making pulp from wastepaper by eliminating most of the ink from the product. More recently, because of the great advances and changes in printing, coating, and converting processes, de-inking has come to mean something different.

It is still a process that is concerned with the process of making a useful pulp from wastepaper, but in doing so it now must function to remove a variety of contaminants such as ink, polyethylene coatings, hot melt adhesives, dirt, and many other non-cellulosic materials.

The technology of de-inking has changed a great deal since it was first introduced, and no one example can be used to exemplify a typical system because what is objectionable in one pulp may not be objectionable in another. Therefore, the complexity and exact nature of the de-inking will vary considerably from plant to plant.

ADVANTAGES OF DE-INKED FIBER

Integrated paper mills with pulp manufacturing facilities have many advantages over those which must purchase all of their pulp. The capital investment in a de-inking plant, although by no means insignificant, is much smaller that the enormous sums required for a conventional wood pulp mill. (3) Therefore, paper mills which cannot possibly incorporate wood pulp production because of expense, location, or other reasons, can in affect become integrated mills by adding a suitable de-inking facility. Although most paper mills with de-inking plants continue to purchase market wood pulp to provide additional volume, or to supply those qualities lacking in de-inked fiber, the de-inking plant makes the mill more independent and often more competitive. Consequently, the use of de-inked fiber is directly related to the cost and indirectly to the supply of market pulp. If there is an abundant supply of market pulp, with subsequent low prices, the use of de-inked fiber will be suppressed. If the supply of market pulp is tight, the opposite is true, and the use of de-inked fiber tends to increase.

In addition, de-inked pulp has the following other advantages:

1) Freedom from complete dependence on market pulp.
2) Reliable source of pulp during times of market pulp shortage,
3) Generally cheaper than corresponding grades of market pulp.

4) The sheet usually has the following physical and optical advantages when de-inked fiber is used;

a) increased opacity

b) less curling tendency

c) less fuzziness

d) better formation

e) better retention of size and fillers

f) softer and less tinny character

Because the stock has already been refined once, it requires comparatively little refining, and thus energy costs for refining are reduced. In addition, in some grades, the addition of de-inked fiber may actually increase the strength, especially in newsprint grades. (9) Garteman (8) showed that by using up to 25% de-inked stock in crepe paper, and 20% in newsprint, that the tensile and burst increased. He also showed that the brightness of de-inked stock can approach that of the virgin stock. Also, the costs of de-inked fiber is often less when compared with virgin fiber. (8)

DISADVANTAGES OF DE-INKED FIBER

There are also several disadvantages associated with using this fiber. They include:

1) Strength may be low, since many of the fibers are shorter
2) Brightness may be low which can definitely restrict its use in certain grades.
3) The stock may be slow, which limits machine speed.
4) There is often a problem due to dirt specks in the wastepaper caused by inks and other non-fibrous materials. Different grades contain different amounts of this, and the de-inking system, and the type of wastepaper used must be matched to produce acceptable quality in the end product.
5) Stickies such as hot melts can cause problems in printing, such as picking, and hickies.
6) The quality of the de-inked pulp, with respect to color, brightness, and strength varies, thus causing problems in controlling the process. It's this variation that is most troublesome, since if the exact composition of the incoming stream is constant, it can usually be made acceptable.
7) The disposal of the waste water, especially from a washing de-inking plant can be a problem, since its BOD is high.

It is axiomatic that de-inked pulp must be cheaper to

produce than corresponding grades of market pulp, or the de-inking plants would eventually shut down. Since there are many grades of wastepaper available for de-inking, depending on the characteristics of the final product, and since these grades vary considerably in price, the exact furnish that is best to use to produce the highest quality end product, at the lowest cost, varys considerably.

WASHING VS. FLOTATION DE-INKING SYSTEMS

The de-inking process itself involves two basic steps. First a combination of chemical, thermal, and mechanical energy in the re-pulping stage causes the ink and other particles to detach from the fibers. Reynolds and Rueben have shown the importance of chemical and thermal energy in the re-pulping process. (20) Other studies discuss disintegration and the simultaneous release of ink particles, depending upon the groundwood content of the paper.

The second step involves a physical separation of the fibers from the ink particles and other contraries. This is accomplished by a variety of combinations of equipment, but they all utilize the same basic principle of screening, centrifugal cleaning, and washing or flotation units.

The last step, washing or flotation, involves the separation of the ink from the ink and fiber suspension. Each has its own group of diehard supporters, but neither system has a clearcut advantage over the other. (50)

washing

Washing de-inking can be defined as a process where

slurried wastepaper has the ink washed from the fiber constituent by passing the slurry over screens and/or through filters, or filter presses of various types. (1) Well known names for such devices include sidehill washers, lancaster washers, etc. The de-inked pulp can be subsequently bleached or cleaned further by washing methods. This type of system has the following advantages; (1)

1) Inorganic filler can be removed and/or controlled, as can the short fiber or fines fraction to some extent. Pulps with higher long-fiber content (hence a stronger pulp) can be obtained. (10)
2) Said to handle variations in wastepaper input quality more easily than flotation
3) Generally has lower capital and chemical costs

This type of system also has the following disadvantages:

1) Yield is generally much lower than with flotation, as fines and pigments are removed during washing. The yield or shrinkage will vary with the type of wastepaper input
2) Higher water consumption and a relatively large volume of effluent water containing ink must be discharged and/or treated (incorporation of an

ink flotation stage in the process water can reduce this)

3) A higher BOD in the effluent stream going to the treatment plant due to the pigments, fillers, and fines present.

A study by Matthew (11) has shown that by operating high consistency counter-current washing, water usage and fiber losses can be kept at a minimum level. Similarly, Guss showed that utilizing a closed water system can result in heat, material, and chemical savings. Problems encountered include corrosion, and chemical and water balances. (12)(9)

<u>flotation</u>

Flotation de-inking can be defined as a process whereby the ink-fiber suspension is aerated in a flotation cell of some type and the ink is carried to the surface where the froth is removed. The fiber can be subsequently bleached or cleaned further.

This type of system has the following advantages;

1) Ink is removed in concentrated form thus reducing or alleviating treatment problems, and helping keep water consumption low

2) The yield is high, typically 85-95% of input wastepaper weight is recovered as de-inked fiber

3) Water circuit can be closed more readily

4) Water consumption is substantially lower than that of most washing de-inking systems now in operation

5) The BOD of the effluent is lower than that of a washing system

6) In some instances it is felt it can aid in removal of hard to remove lightweight contaminants by floating them out

This system also has the following disadvantages;

1) Inorganic filler (china or kaolin clay) is not removed, nor are fiber fines. Control of these elements is said to be difficult by flotation alone. Fines and fiber fragments can decrease strength. (10)

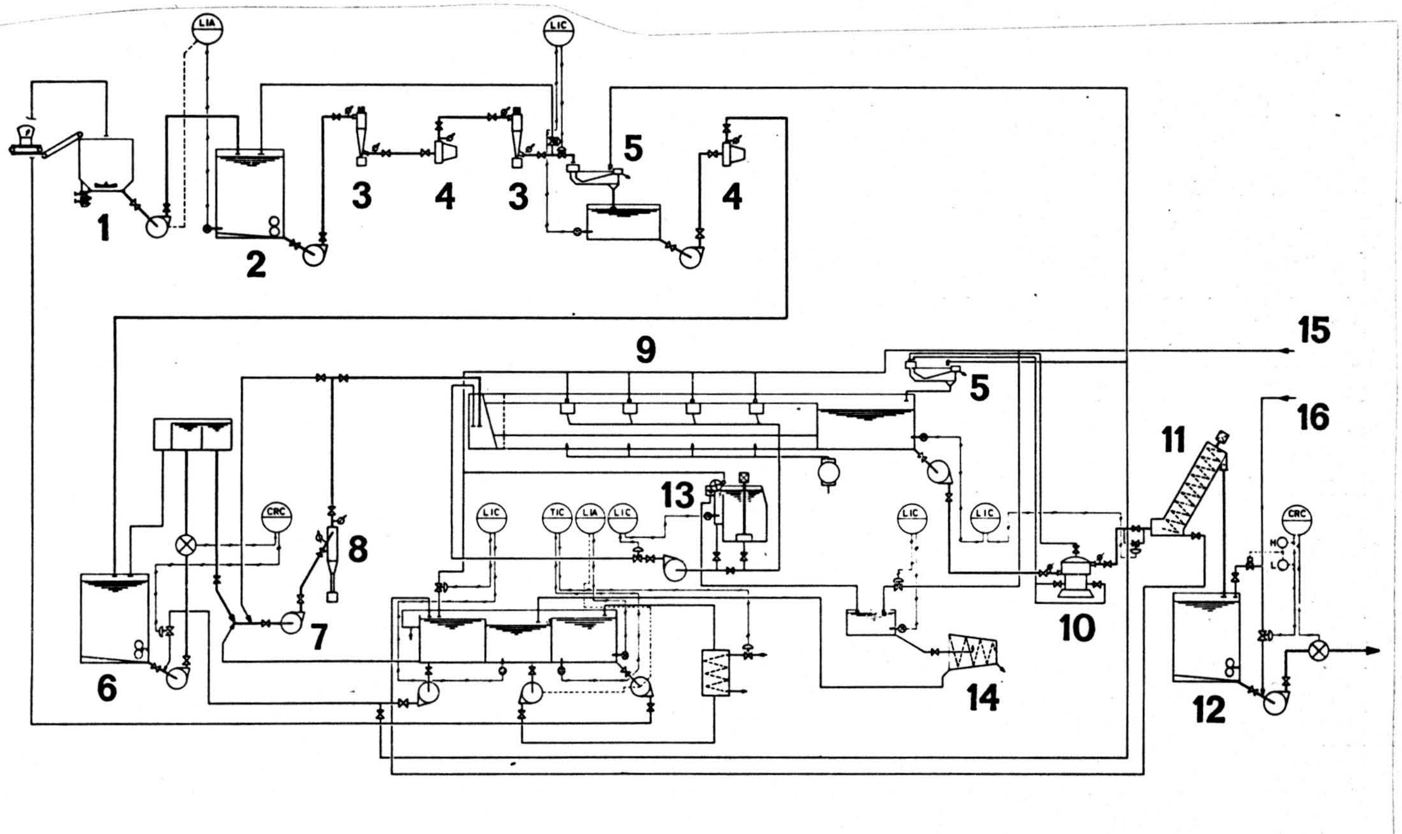
2) Generally has higher capital and chemical costs

Clewley (10) however suggests that if there are stringent effluent restrictions and/or constraints on water availibility, the costs for added waste treatment and the capital cost of the washing installation may actually be higher

In addition, Clewley indicates that chemical costs can be higher for washing. Hanson (13) and Clewley show that the energy costs for a flotation system can be lower due to its lower pulping temperature and reduced steam usage. Clewley

shows further that the labor, floor space and overhead costs are similiar for both processes.

In reality, there is no one system that can represent all the various systems in operation. However they all contain the basic elements of a pulper, screens, cleaners, and the flotation cells. The schematic (figure 1) is an example of one such system in operation and will serve to illustrate what equipment most systems have in them.



1. Pulper
2. Dump Chest
3. High Density Cleaner
4. Deflaker
5. Vibrating Screen
6. Intermediate Chest
7. Mixing Pump
8. Low Density Cleaner
9. Unicell (Primary Stage)
10. Pressure Screen
11. Screw Press
12. Storage Chest
13. Flotation Cell Type FZ (Secondary Stage)
14. Decanter Centrifuge
15. Fresh Water
16. White Water

combination de-inking systems

There are several new plants that combine elements of both flotation and washing into one system to take advantage of each systems strong points. (1) (2) The trend in the future seems to be in this direction if the economics of the increased equipment cost can be justified. There are currently three such systems in operation in North America. (2) Studies by Cruea indicate that the greatest effectiveness is achieved when flotation and washing are used in combination. (49) Flotation removes some specks that are too small for screening and those too large for washing out.

DETACHMENT OF PRINTING INK

All de-inking systems begin with some type of operation that functions to disintegrate the wastepaper and to simultaneously release the ink particles and other non-fibrous materials from the fibers. In simple terms, it's a combination of chemical, thermal, and mechanical action.

Some systems merely break down the ink particles and disperse them in the sheet. (32) (33) (34) By a combination of heat and mechanical action, the size of the particles is reduced so much that they are no longer visible to the eye. (15) (17)

S.D. Welds (14) mentions six necessary ingredients for effective repulping in a standard washing type process:

1) Alkali to saponify the ink vehicle
2) Detergent-sulphonated oils and fatty acids and complex phosphates
3) Dispersing agent to prevent agglomeration of pigment and to emulsify the non-saponifiable mineral oil or wax from the ink. This is true in

the case of newsprint where the ink is made of pigment and mineral oil generally

4) Softening agents such as kerosene dissolves gelsinite and synthetic resins

5) Selective absorptive agents to prevent pigment redeposition (e.g. by filler clay)

6) Miscellaneous chemicals to prevent calcium soaps (important with hard water) e.g., tetrasodium pyrophosphate (TSPP) or hexasodium metaphosphate

It must be kept in mind however, that in some grades, if the mechanical and thermal action are too intense, the ink will become finely divided and will adsorb on the surface of the fillers present. This can interfere with brightness developement, especially in flotation de-inking.

CHEMICAL PARAMETERS

Chemical formulations vary considerably from system to

system depending on many factors such as the waste grades, the de-inking process itself, the equipment available, and the end product desired. A typical formulation for groundwood stocks is as follows; (18)

Sodium peroxide, Na_2O_2	%*	2
or = $NaOH + H_2O_2$		
Sodium Silicate	%	4
foamer	%	0-0.25
collector	%	0.3-0.8
final pH	>9.5	

*- based on weight of dry fiber

This formulation consists of various alkalis and surface active agents. In addition, on especially hard to de-ink wastes, organic solvents such as dichlorobenzene are sometimes used. (19)

Alkali

The primary affect of an alkali such as Caustic Soda is to increase the swellability of cellulosic fibers. (20) Since only 4-8% concentration is generally used, there probably is limited penetration into the cellulosic miscelles (unless the inter-crystalline structure has been previously affected). Exposed parts of the fiber may be solubilized and therefore cause some loss or degradation of fibers. This is due to cellulosic breakdown which is related to the condition of the fibers, alkali concentration, temperature, and duration of the

of the de-inking operation. (3) (22) (21)

The alkali also saponifies the binders in conventional inks, or at least weakens them to such an extent that their capacity to adhere to the fiber is overcome. (3) Matlingley (23) has a somewhat different opinion from most. He states that the alkali merely produces the stabilized ink-fiber suspension and that it does not saponify the ink vehicle to any degree. Thus the printing ink pigments are removed with their mineral oil or resinous binders from the fibers. He's referring only to inks such as newsprint inks, which have no saponifiable constituents.

Bechstein (21) also discusses the role of alkalis. He states that in addition to acting as saponifiers, it is possible to prove that they have a favorable effect on, and influence the detachment of, the printing ink from the fibers. He investigated the affect of the kind of alkali and the pH on the whiteness of the de-inked pulp. In general an improvement is recorded in the de-inking effect owing to a greater detachment of printing ink as the pH increases. The theory is that the electrostatic repulsion between the fibers and the particles of impurities is increased by the absorption of OH^- ions.

The action of alkalis upon wastepaper fiber is further complicated by large quantities of lignin which may be present from groundwood papers. In the case of some book and magazine papers, the groundwood content may be as high as 50% so the average lignin content may run as high as 12-15%. (3) Lignin is highly reactive and is particularly susceptible to oxidation. Alkalis in general darken lignin, an exception being alkaline

peroxide solutions which also serve as limited bleaching agents.

In the de-inking of high groundwood containing papers, high alkalinity or pH can cause excessive yellowing or color reversion. (3) (33) In this case, various less severe alkalis such as Calcium Carbonate, Sodoum Silicate, or Sodium Peroxide are used. (24)

NaOH

Caustic Soda is a strong alkali that at high concentration can attack and break down the cellulose. It is by far however, the most common alkali used to de-ink wastepaper. (2) (24) Generally it is not used in excess of 5% (3), and has been used as low as 2%. In extreme cases, 8% has been used. If used on high groundwood content pulps, care must be exercised to avoid yellowing to the pulp which will occur if NaOH is used in too high of a concentration.

Sodium Silicate

Sodium Silicate is also recognized as a particularly suitable de-inking aid, especially for waste containing mechanical pulp. (21) (25) (26) It acts as a penetrant and dispersant. Waste paper with a high groundwood content also has a high lignin content (3) and Silicate is often used in combination with Na_2O_2 to prevent the pulp from yellowing. In this case it would be used in the range of 5-6%. The Na_2O_2 also bleaches the fibers slightly, by the action of the active OOH^-. The water glass stabilizes the active oxygen of the peroxide by allowing the pulping process to continue at a lower pH than NaOH would, or in other words, it acts as a buffer. (3)

Bechstein (21) indicates that the increase in whiteness caused by the use of Sodium Silicate is not due solely to different yellowing phenomenom. He states that the Silicate is a better de-inking agent than the caustic soda at the same pH. The use of Sodium Silicate in combination with Silicic acid is recomended as this forms a colloïdol solution which allows good removal. His results show that Sodium Silicate should be used for optimum detachment of printing ink during pulping and is preferred to phosphates, carboxylates, and hydroxide. The normal range is up to 3% if used on groundwood paper in conbination with NaOH or NaOH and Na_2O_2.

Sodium Peroxide

Sodium Peroxide is a dispersing, saponifying, and bleaching agent that is used extensively to pulp furnishes containing a high amount of groundwood. Basically it serves two purposes. (3) First, it is active chemically in converting glue, casein, starch, and certain oils into water soluble types, thereby aiding in the dispersion of inks, coatings, and sizing materials. Secondly, it improves the brightness of both groundwood and chemical pulps, as opposed to the noticeable darkening which occurs when groundwood is cooked in a strong alkali solution without peroxide. Up to 2% peroxide is generally employed, usually in combination with Sodium Silicate. Magnesium Sulfate is sometimes added to stabilize the peroxide against catalytic decomposition due to contaminants such as copper, manganese, or iron. Hydrogen Peroxide with caustic soda can be substituted for Sodium Peroxide if facilities for handling the Sodium

Peroxide are not available.

Since the peroxide bleaches the pulp slightly, a noticeable brightness gain can often be observed. Vanderhoff showed that Sodium Peroxide was superior to NaOH as a de-inking chemical, because it elimanated more ink specks and gave a better color. It appears effective in de-inking those papers such as Ultra-violet cured inks that NaOH will not. (48)

In low groundwood containing papers, the benefits of peroxide diminish as its higher cost becomes the overriding factor.

<u>Detergents</u>

Detergents also play a major role in the detachment of the ink from the fibers. This group of materials is effective in dispersing the colours and forming the foam needed for the flotation process. Most anionic surface-active agents have a strong tendency to foam, which generally makes them undesirable for the flotation process. (27) They are particularly useful in improving the detachment of printing inks which saponify. (21) Alkyl sulphates are less effective than the non-ionic detergents such as slightly ethoxylated nonylphenols, which have proven to be the mostefficient for this purpose. (21) The non-ionics have the following advantages;

1) Maximum surface penetration and therefore the greatest activity even at the low concentrations which are normally used.
2) They work particularly well in emulsifying and dispersing the oily and fatty impurities which are derived from the printing inks during pulping.

The hydrophobic olefin part of the surfactant has an affinity for the oily impurities and the result is the two molecules form a highly polar (and thus readily soluble) absorptive compound.

These emulsifiers, or detergents, if used in excess concentration, hinder the agglomeration of the ink by the collecting agent. Thus they are used at a concentration that will cause minimal reduction in the surface tension in the flotation cell and thus avoid destroying the agglomerates. (21) Bechstein (21) recommends that the optimal application rate is 0.1% to 0.2%, in relation to the dry pulp. This is equivalent to about 0.02 to 0.04 grams per liter. Thus Bechstein concludes that the combined use of alkalis and non-ionics is the best method for detaching printing ink.

Other detergents that have been used to aid de-inking include alkyl benzene sulphonate, alkyl phenol-polyglycol ether, and ethoxylated fatty acids. (28)

In the United States considerable work has been done by Garden State Paper Company. They suggest that wastepaper can be de-inked by using a biodegradeable de-inking agent which is composed of an ethoxylated aliphatic mono-ol (29), and also by the use of non-ionic detergents such as ethylene oxide adducts of alkyl phenols. (30)

Physical Parameters

In the re-pulping operation that is an integral part of de-inking, there are several physical parameters to consider

that effect the de-inking process. It must be kept in mind that although adequate dispersion of the ink and fiber is the goal, it is equally important to avoid excessive mechanical, thermal, or chemical action prior to screening. Such forces can reduce dirt to such fine particles that screens do not reject. them. It can also destroy the cellulose fibers, and reduce the ink particles to such a fine size that they deposit on the fibers and fillers. (31)

Consistency

The consistency in the pulper that is utilized industrially varies considerably from low density (5-7%) to high density (up to 35%). (16) High density cooking has the advantages of using less heat and chemicals, but sometimes has a higher labor cost and may require special equipment for handling the materials in process. In addition, they are at a disadvantage because of liquid agitation and greatly reduced shearing and emulsifying action. The forces involved may be very large, but there is more limited mechanical action because of the comparatively small movements of the stock. Other claims rebuke this theory, claiming that wastepaper such as newsprint should be pulped at a consistency as high as possible to promote fiber to fiber rubbing. (32)

From a chemical viewpoint, the reactions may be different at a high concentration, and generally more favourable; from a mechanical viewpoint the equipment should be smaller in volume for the same capacity. The difficulty in pumping such thick stock must also be considered. (3)

Thus generally it is believed that increasing the consistency is beneficial up to the point where agitation becomes impaired. It sometimes results in decreased time, improved ink removal, and generally better quality. High consistency pulping also aids more in defibering the stock. The exact consistency that is best to use varys depending on equipment, wastepaper, and product desired. It's also governed by the filler content of the wastepaper since it does not affect the pulping process.

Temperature

The temperature in the pulper is another variable affecting the de-inking operation. Temperatures in excess of 212°F have been used in pressurized pulpers to de-ink wet strength papers by acid hydrolysis; however it is generally found unnecessary in alkaline cooking. The temperature depends on the wastepaper used, the chemicals, type of bleaching operation, and on the final type of de-inked pulp desired. Generally, ledger grades of wastepaper are cooked at 160-210°F, and on high groundwood content papers, lower temperatures are used.

It has been found that increasing the temperatures reduces the cooking time, especially at the higher temperatures. (3) This is because heat softens ink and other non-fibrous materials, thereby increasing the effectiveness of chemical action, dispersion by means of abrasion and shearing action, and stabilization in the colloidol condition. High temperatures also favor rapid defibering.

It must be emphasized however, that high temperatures do not apply to high groundwood papers. Such papers de-ink and

defiber better at the temperature is decreased. (3) Temperatures of 100-160°F are common. If the temperature is increased over 160°F, color reversion occurs, with an associated loss in brightness. (33)

Time

As is the case in other factors affecting the de-inking operation, the time of cooking varies considerably. Many mills have found it advantageous to have a soaking period with chemicals prior to the actual cooking. (3) Escher Wyss (18) suggests a 20 to 30 minute pulping time for woody and woodfree wastes, with an additional 1.5 to 2 hour retention time in the dump chest prior to flotation. Galland (34) suggests that a shortened pulping cycle can produce de-inked pulp of an increased brightness. He studied the affect of pulping time on old newsprint and found that pulp de-inked for ten minutes and then floated had a brightness that was higher than stock that was pulped for 20 minutes with a 30 minute soak time. Therefore he concluded that in some cases it is possible and even advantageous to reduce the pulping time. Degussa (35) and Ortner (26) talk of preimpregnation with chemicals for approximately one hour at a stock consistency of 30% prior to pulping. This shortens the slushing time, and also allows the pulp to be slushed at normal temperatures.

Thus the time that is best to use is the minimal time that produces a de-inked pulp of the desired quality.

FLOTATION

Flotation Theory

Flotation depends on the relative wettability and/or electrical charges of surfaces, but the mechanism has been the object of considerable speculation. Various hypotheses have been proposed along with some experimental evidence to support each theory.

Initially it was recognized that oil promoted adhesion of particles to bubbles and this was rationalized by assuming the oil adhered to both particles and bubbles thus bonding them together. The presence of oil in the gangue added evidence to this view. (7) Taggart (36) suggested that bubbles were formed directly at the particle surface as a result of supersaturation in low pressure regions created by vortices of the impeller blades upon agitation. Gaudin (5) however indicated that rising air bubbles merely collide with particles and adhere to those which have an affinity for air.

Additional theories proposed include the chemical or solubility theory and various adsorptive theories involving attachment of the collector as an ion, a molecule, a monolayer, and a multi-layer. The solubility theory postulates the formation of an organomettalic compound on the mineral surface which is less soluble than the mineral itself, and can thus be floated, whereas materials that form more soluble compounds are not floatable. (4) (7)

Recent investigations employing radioactive tracers and electron diffraction techniques have contributed additional information (4); however no single theory has been fully accepted. Currently more importance has been attached to contact angle, surface tension, interfaces, and structure of the flotation reagents used in the process. The major technical problems are concerned with chemical control of the material surface.

A prerequisite for the physical process of selective flotation is differing wettability of the components to separated in a system- e.g. a liquid/solid system. The process of de-inking by flotation relates to a system of fibers, fillers, and ink particles in an aqeous suspension. These have to be separated' from each other to such an extent that the ink particles rise to the surface while the fibers remain in the suspension. This is achieved because the ink particles have a poorer wettability than the fibrous materials. (28)

To get a selective process for removing ink particles by flotation, a suitable flotation agent is added. In its simplest form, this agent may be a soft soap. These agents are characterized chemically by a long chain molecule containing hydrophylic and hydrophobic groups. The hydrophylic groups of the soft soap act as frothers and reduce the surface tension and this promotes foaming and bubble formation. The hydrophobic groups react with the hardness causing salts in the water, and form precipitated flaky calcium soaps. Therfore we also speak of "flake flotation", since these sticky calcium soaps act as the collectors.

By suitable selection of the frother and collector many materials can be floated out such as minerals in the mining industry, and contaminants in wastepaper.

Surface Chemistry

To further explain the relationships of contact angle and wettability and to determine the theoretical limitations of the flotation process, the physical chemistry of interfacial phenomena must be examined.

If a particle is to float, the total upward pull of the meniscus on it must balance the apparent weight of the particle. (37) The vertical force applied to a particle can be expressed by equation (E-1):

$$\text{(E-1)} \qquad \gamma_{A/W} \cdot \cos\theta \cdot \text{(particle diameter)} = V(d_p - d_w)g$$

where;

$\gamma_{A/W}$ = surface tension of water phase

θ = contact angle on vertical side of particle

d_p = density of particle

d_w = density of water

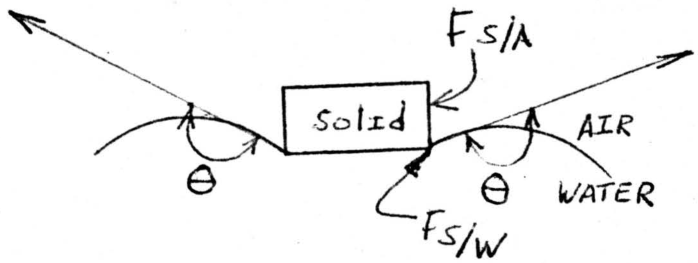
V = volume of particle

g = gravitational constant

The relationship between the $\gamma_{A/W}$ and θ can be described graphically (G-1) and mathematically (E-2);

$$\text{(E-2)} \qquad \gamma_{A/W} \cos\theta = F_{s/a} - F_{s/w}$$

(G-1)



$F_{s/a}$ = Helmholtz free energy of solid/air interface

$F_{s/w}$ = Helmholtz free energy of solid/water interface

Since $F_{s/a}$ and $F_{s/w}$ are sensitive to surface active agents, the condition for floatability can easily be changed. Additives such as collectors act by absorbing onto the surface of particles and them making them floatable by reducing $F_{s/a}$, and by (E-2), cos θ decreases and θ increases. (7)

The maximum size allowable for an ink particle to float can be calculated by rearrangement of (E-1);

$$\frac{\gamma_{A/w} \cos \theta}{(d_p - d_w)} = V = DH \qquad \text{(E-3)}$$

D = cylindrical particle diameter

H = cylindrical particle height

In a series of substitutions, Vanderhoff showed that flotation can theoretically remove particles far larger than the largest ink particles observed. (38) By substituting θ with the minimum angle needed for flotation, i.e., 50°, this gives $\gamma_{A/w}$ = 50 dyne/cm as a minimum value. This corresponds to an ink density of 1.2 gm/cm^3, and the DH = 0.66 cm^2. If you

assume that D=H, then D=H= 0.8 cm, Although D may not equal H. Therefore set H = 5μ (the ink film thickness) and by (E-3) D = 1100 cm for an ink film density of 1.2 gm/cm^3. These values are much greater than the size of standard ink particles observed in waste paper. (38)

FIBER AND INK SEPARATION

Chemical Parameters

As stated before the principle of selective flotation relies on the physical differences in wettability to separate fibers from the ink, dirt, and other contaminants. After the preliminary stages of pulping and screening, the stock is diluted to approximately 0.8% consistency and introduced into the flotation cell along with the chemicals.

The chemicals required are basically surface active agents and modify the surface tension of the system and the wettability of the particles. These chemicals are generally called foamers and collectors.

Most surfaces of solids exhibit strong polar surfaces and are thus readily wet by water, and therefore lack an affinity for air. Surfaces free of unsaturated bonds lack affinity for hydrogen or hydroxyl ions in water, and preferentially attach to air. Consequently, successfull flotation of several minerals has been due to the developement of chemicals that form water repellant surfaces either by reaction or absorption. The reagents are usually heteropolar organic compounds selective to specific surfaces. Success in flotation has also been augmented with reagents that form stable foam upon mechanical action. These chemicals or flotation aids are classified as either collectors, frothers, or modifiers and work together to promote bubble-particle attachment, and thus selective

separation of solid particulate matter from a liquid phase.

Flotation Aids

Collectors

Collectors are the heart of the flotation process since they are the reagents which raise the contact angle on the solid particle. Collectors, like frothers, are usually organic, heteropolar compounds with a polar and non-polar radical. (4)

To have a good affinity for solid particles, collectors must have polar, ionic, or chemically active groups as a portion of their molecular structure. These molecules are long chain molecules that contain a hydrophobic end- the negatively charged fatty acid portion, and a hydrophilic end- a positively charged functional group. (28) The hydrophobic group reacts with the hardness causing salts in the water and forms precipatated calcium soaps. This chemical attaches to the fiber, and attaches to the air bubble, thus connecting the ink particle to the air bubble. This increases the hydrophobic character of the pigment, and since the air bubble is buoyant, it and the ink particle float to the surface. (22)

Bechstein showed that collector effectiveness is greatly improved as the length of the carbon chain increases. (21) Also, more favorable results are obtained with unsaturated long chain fatty acid soaps than with a saturated fatty acid soap. The best results were obtained when unsaturated long-chain carboxylates are used with approximately 10% saturated. The increase in hydrophilic and polar tendency of the unsaturated

fatty acids is thought to stabilize the collecting flakes in the liquid. This prevents the flakes from rising too quickly to the surface of the liquid and therefore encourages the formation of froth.

Collectors are classified as either anionic, cationic. or nonionic. Anionic collectors include xanthates, fatty acids, dithiophosphates, sulphonated or sulphated fatty acids, sulphonated oils, glycerides, and various alcohols. Cationic collectors are amines and amine salts. Neutral hydrocarbon oils are nonionic reagents. (4)

Water glass (Sodium Silicate) can also function as a collector. It hydrolyzes in water and causes free silicic acids to flake out with the hardness salts as insoluble silicates. The silicate flakes have an active surface and therefore are well suited as printing ink collectors.

The concentration of collectors are usually quite low, around 0.2 to 0.5 gm/liter.(0.3 to 0.8 %).(18) (21) Maximum flotation will be achieved whenever all the hardness agents are flocculated and there is a slight excess of free surface active soap. A large excess of soap does not increase the flotation affect, rather it reduces it. The strong attraction between the non-polar chains of the soap molecules causes surface active molecules to deposit on the precipatated calcium soaps (the collector) so that the hydrophilic polar groups of the deposited molécule turn to the aqeous phase. This reduces the absorption of the agglomerates and consequently reduces the flotation affect. (21)

Foamers

The main purpose of frothing agents (or foamers) is to procuce a froth capable of supporting the solid laden air bubbles until removed from the flotation unit. These agents provide a covering film on the bubble which imparts a temporary toughness until further stabilization is established by adhering mineral particles to other adjoining bubbles.

To create froth the agent must lower the surface tension of water. Most organic compounds demonstrate this ability, but those effectively used are limited since frothers should be low cost, readily available, safe, and effective in low concentrations. Common examples are pine oil, cresylic acid, and certain synthetic alcohols. These are all organic heteropolar compounds with the non-polar radical repelling water while the polar end attracts water. The molecules concentrate at the bubble walls with the polar end adhering to the water phase, and the non-polar end turned toward the gas (air) phase. This distribution of frother molecules at the bubble surface also imparts the required elasticity to enable the rising bubble to burst through the top layer of water and emerge at the air-water interface intact and unbroken. (4) Gaudin (7) found that the frothing ability of organic compounds increases with increasing length of the hydrocarbon chain, up to 7 or 8 carbon atoms. Therafter the frothing ability decreases. Ortner (28) agrees with this, and he proposes that collectors and foamers are long chain molecules that contain a hydrophobic and hydrophylic end.

pH

The affect of pH on the flotation process has been investigated by Miller. (4) He found that the pH had a noticeable effect on the volume of entrained air obtained, with a pH of 9.0 the best. The pH of the system also influences the effectiveness of the flotation reagents. Escher Wyss recommends a pH in the flotation cell of 8-9. (18) Raimondo (40) studied the effect of varying the pH on the flotation of illustrated magazines (65% groundwook, 35% bleached pulp, ash content 24%) and newsprint (65% groundwood, 35% bleached pulp). He found that below a pH of 5, large bubbles formed and frothing was at times uncontrollable. With a pH above 11, a thick dense froth was observed with the formation of very small bubbles. The high pH also yellowed the pulp. He showed that a pH of around 9 was optimum, and that close attention should be paid to the pH because if it drops below 8 or so, a sudden brightness drop can result.

Water Hardness

The hardness of the water can have an important effect on the success of the flotation process according to Bechstein. (21) Maximum flotation will be achieved whenever all the hardness agents are flocculated and there is a slight excess of free fatty acid soaps. If the optimum hardness is achieved, the surface active soaps, which play the role of foaming agents and stabilizers, are precipitated out and very large flaky structures result. These are hard to remove and may also entrain fibers and increase fiber loss. Research indicates that

optimum hardness is about 7 deg German (125 ppm) Ortner supports this theory. He states that in soft water, the flocs formed by the precipatated soap, to which the particles attach themselves, are lacking. (39) Raimondo has a somewhat different idea, and states that the water hardness has little effect on brightness, unless it's zero, which results in no flotation at all.

Physical factors

There are various physical factors that effect the operation of a flotation cell. In order to understand what they are and how they are interrelated, each will be examined separately.

Particle Size

Fine particles in the near-colloidal size are difficult to recover by flotation. Part of the problem is mechanical difficulty in contacting the air bubbles. Very large particles are also difficult to float out, but can usually be removed by screening.

According to Bechstein (21), the frequency of non-floatable ink particles is highest in the area below 5μ, and decreases with increasing particle diameter. He explains that Brownian movement counteracts the adhesion of the particles to the air bubble, if its less than a 5μ particle. Thus agglomeration becomes important. Studies by Mack (41) show that froth from a flotation unit contains ink particles of 2μ to 10μ in size.

He also found that particles of greater than 25μ aren't floated out to any degree and are not elimanated. Those less than 2μ in size were unpredictable and in general were floated out. Gaudin (7) mathematically relates the upper limit for squat cylindrical shaped particles that can be removed by flotation to the specific gravity and contact angle. Surface wettability is thus a very important parameter, as it governs the contact angle between air and the particle. If the contact angle of a particle is nil water wets the solid in preference to air and air-solid contact is impossible. An angle of 180° represents wetting of the mineral by air to the exclusion of water. No solid is known to give a contact angle larger than 110°. The contact angle can be controlled somewhat with the addition of flotation reagents, which alter the surface wettabilities. Flotation has an advantage here over washing because it is not as sensitive to ink particle size and also because it can remove particles far larger than the largest size ink particles observed in the de-inked paper specimens. (42)

Time

The effect time in the flotation cell has been studied by Raimondo (40). He found that the brightness of the de-inked pulp increased as the flotation period is prolonged, e.g. by the addition of further cells. He also found that the brightness values of the two sides of the sheet approach a common value with increasing time. This is due to the fact that ink, filler, and fines present in the stock are eliminated more efficiently during a longer period of time, until eventually

only the fibers are left behind. Thus this phenomenom of similarity of brightness values could be used in certain cases as an indicator or measure of de-inking efficiency.

Temperature

The temperature in the flotation cell has a marked affect on the surface tension of the suspension. (40) The surface tension decreases with temperature. At low temperatures bubble formation on the surface is poor and consists of a relatively thin layer. As the temperature is increased, the bubble formation and frothing improves, resulting in increased brightness.

Bubble Size

Another parameter of interest is bubble size. Arguments for both large and fine bubbles have been presented in the literature. Finer bubbles provide more surface area per unit volume of air and hence more solid particles can be accomodated at the air interface. However, energy is required to disperse gas and finer dispersion requires more energy. Raimondo (40) found that the quantity of air present in the stock had little effect once a minimum level was reached. If a maximum value was exceeded, surface disturbances resulted in indffective flotation.

Affect of Fillers

Several references are found in the literature to the use of pigments and fillers as absorbing media for the ink particles present in the solution. It is maintained that these agents prevent the ink particles from readsorbing onto the fibers.

Thus papers having a high percentage of fillers should experience a brightness gain during the flotation process. Raimondo (40) did a study on this and concluded that the increase in brightness obtained by the addition of the fillers was due to the inherent whiteness of the filler itself (in this case china clay) and not to the adsorption of the ink particles onto the fillers. Other sources claim that fillers probably help under some conditions but are of no value under other conditions. One source (3) hypothesizes that since they are effective in stabilizing colloidal dispersions, it seems likely that they help to some extent. Some fillers are more effective than others; Bentonite has been found to be of value in deinking. (41), and diatomaceous earth has been found helpful for cleaning small quantities of asphalt or waxy particles when used with kerosene.

This area is one that has a wide difference of opinion concerning it, and very little hard data published to back anything up. Most operations merely throw in the filler without really knowing whether or not it really affects anything.

DE-INKABILITY OF NEWSPRINT

The ease with which a wastepaper stock can be de-inked depends on various factors. These include the type and amount of contaminants present, the type of wastepaper, the type of ink, and the process and equipment used to de-ink it. The de-inkability is also related to the nature of the end product desired. Or, in other words, what is objectionable in one pulp may not be objectionable in another. As a result there are a great many kinds of de-inked pulp produced, of varying quality, and of varying degrees of difficulty.

When referring to the de-inking of high groundwood papers, we are referring to that grade of wastepaper that has a majority of the furnish made by the grinding of the wood via a grindstone. These papers are exemplified by news, so called "pulp magazines", and a variety of other magazines printed or machine coated groundwood papers.

Since these papers contain significant portions of lignin, they must be de-inked under milder conditions to avoid yellowing.

In order to better understand the de-inking of newsprint, a discussion of the ink that has to be liberated from the fiber would seem in order.

Inks can be classified by major printing processes and the amount of film likely to be present on the sheet, as follows:

PROCESS	SINGLE FILM THICKNESS-μm
Letterpress	4-6
Litho offset	1.5-3

Ink Chemistry

Inks are also classified by their vehicle chemistry or method of drying. There are several major methods of drying, and these include absorption, evaporation, oxidation, radiation curing, and heat polymerization.

Newsprint inks dry by absorption.(44) They generally consist of a carbon black pigment dispersed in a mineral oil. It does not really dry or convert to a solid, but depends on the wicking of the liquid portion of the vehicle into the paper to cause an increase of viscosity of the ink surface. This is why newspapers will leave a black residue on your hand.

The construction of such inks varys slightly depending on whether it's a letterpress or offset operation, as is shown below by a typical newsprint ink formulation;

Letterpress News		Offset News
9-15	pigment	10-18
80	mineral oil	20-50
--	H/c resin	10-30
2-5	H/c pitch	2-5
--	mineral seal oil	20-30

These inks are totally hydrocarbon in construction and are not subject to saponification with alkaline chemical treatments. Thus removal depends entirely on emulsification and/or mechanical removal.

Various varnishes such as linseed phenolic varnish and/or rosin varnish can also be used, in combination with furnace

black. A typical formulation for web offset news ink is shown below; (45)

parts	
16	furnace black
5	toner
15	linseed phenolic varnish
24	rosin varnish
20	mineral oil (130 poise)
20	light mineral oil

Work done by Ortner illustrates the affect of the particle size of the carbon black; its size affects its wettability. He found that the carbon black used in newsprint inks in the United States was harder to float out than European carbon black. (46)

Generally newsprint is not an especially difficult paper to de-ink, and only requires mild pulping conditions to liberate the ink.

BLEACHING

Bleaching of wastepaper can be done in the pulper or after it has been cooked and washed or floated. The type of bleaching varies and depends on the wastepaper, process, equipment, and end product desired. (3)

Most mills in North America bleach with Hypochlorite (2) unless they de-ink high groundwood content papers. If this is the case, Sodium Hydrosulfite, Zinc Hydrosulfite, Sodium Peroxide, Hydrogen Sulphide, or Hydrogen Peroxide can be used to help elimanate reversion problems. (43)

For higher brightness pulps, multi-stage bleaching is used. The most common is C-E-H (chlorination, caustic extraction, hypochlorite).

If the pulp is bleached in the pulper and cleaned via flotation, calcium hypochlorite instead of the more common Sodium Hypochlorite is sometimes used, because the calcium ion aids in bubble formation and collector efficiency.

PRESENTATION OF PROBLEM

In the flotation de-inking process there are several key variables, both physical and chemical, that affect the performance of the flotation process.

The purpose of this thesis is to examine one such parameter; the utilization of pigments or fillers as a flotation aid.

The use of such pigments is an area that is characterized by little hard data, and a very incomplete understanding of the mechanics of how they function. Most of the time, they are added merely because they are suspected of aiding flotation, and people continue to use them because they do not desire to change a formulae that has proven to be successful in the past.

The most common pigments mentioned are bentonite clay and diatomaceous earth. These pigments are theorized to act as an absorbing media for the ink particles. The ink-filler agglomerate is then easier to float out than the ink particles alone.

EXPERIMENTAL

EXPERIMENTAL DESIGN

The objective of the experimental design is to determine the effect of pigments in the flotation de-inking of newsprint. In order to accomplish this goal, the procedure was divided into two phases. Phase I was of a more preliminary nature, and its goal was the developement of an acceptable de-inking formulation. This formulation consists of a combination of chemical, thermal, and mechanical energy inputs in the pulping and flotation of the stock. Some parameters such as temperature and pH are quite well defined in the literature, and thus did not need extensive investigation. Other parameters, such as the chemicals used, and their concentrations, have only general guidelines available in the literature. Therefore it is difficult to determine what combination of these parameters will suffice. Thus Phase I is designed to evaluate various combinations to find one that performs well and produces a de-inked stock of acceptable brightness and one that's relatively free of ink specs. The goal is not to find an optimal formulation but merely to find a combination that will produce an acceptable product. Once a good formulation is found it then will be tested repeatably to insure that it will produce consistent results if all parameters are held constant. Once reproducibility is established, Phase II, which is the determination of the effect of pigments in the flotation de-inking of newsprint, will commence.

Several references in the literature suggest that pigments, if added to the stock, will aid in the flotation and removal of the ink and impurities. Phase II is designed to show whether this is the case. The pigments used are pigments mentioned in the literature as being used previously for this purpose. They are talc and diatomaceous earth.

In order to determine the effect of their addition, the pigment will first be added prior to flotation in the pulping stage. The stock will then be de-inked and Buchner funnel pads made. The brightness will then be measured. Stock will then be de-inked without the pigment being added before flotation. The pigment will be added after flotation prior to the making of the pads. The amount added will be based on the amount actually present in those sheets which had the pigment added before flotation. This amount will be determined by percent ash tests.

By comparing the brightness of the pads having the pigment added before flotation to those having it added after, the effect of the pigment can be determined. If the before and after cases are the same, then the pigment did not have any effect. However if the pads with the pigment added before flotation have a higher brightness than those which had it added after, it can be concluded that the pigment serves as a flotation aid and improved flotation and ink removal.

EXPERIMENTAL PROCEDURE

The experimental procedure was divided into two parts,

which have been labeled Phase I and II. Phase I is the development of the de-inking formulation. Phase II is the determination of the effect of pigments in the flotation operation.

Phase I- Developement of the de-inking formulation

In order to operate the flotation cell in an acceptable manner, to produce a de-inked stock of acceptable quality, a suitable combination of energy inputs needed to be determined. General guidelines for such parameters as chemicals, temperature, and pulping time are available in the literature but the exact operating conditions vary a great deal from operation to operation depending on many factors such as the type of wastepaper, the end product desired, and the equipment available.

Flotation de-inking consists of three stages, pulping, soaking, and flotation. Each stage has several parameters which effect its operation. Phase I was designed to study several of these parameters in order to find an acceptable combination.

The pulping stage consists of mechanically agitating the stock in some manner in order to promote defibering of the stock and removal of the ink from the fibers. It also consists of the addition of chemicals and heat to aid in this removal.

The pH and temperature are well defined and were not studied. The pulping time, soaking time, chemicals and their concentrations were all investigated as these are not as well defined.

The chemicals utilized and their concentrations are not as well defined as some of the other parameters and their use varys a great deal. Since they have a significant effect on the de-inking operation most of Phase I consisted of varying the chemicals used and their concentrations. Several chemicals mentioned in the literature and commonly used industrially in the flotation de-inking of wastepaper were looked at. These include oleic acid, stearic acid, CF-10 (a Rhom and Haas dispersant), and sodium silicate. Many flotation de-inking operations use one or more of these in combination.

Most mills de-inking groundwood containing wastepapers use sodium peroxide. It bleaches the fibers slightly and as a result can produce a higher brightness pulp. However since the objective of Phase I was not optimal brightness developement, but merely good ink removal, it was decided not to use any bleaching type chemicals. If a higher brightness were desired bleaching could always be done after flotation.

Another chemical that was investigated was potassium soap. This was manufactured by reacting oleic acid and stearic acid with potassium hydroxide and heat. This process converted the acid form to the soap. It was proposed that this form might function as well as or better than the acid form. The soap consisted of 45% oleic acid, 5% stearic acid, and 50% distilled water.

The pulping time, and soaking time were also studied to find a good operating range for these two parameters. Common industrial values vary a great deal with a total of up to three

hours used in some cases.

The temperature, time, and pH in the flotation were well defined in the literature and therefore were not studied. They were set at commonly used values and not varied. (see Table I)

The hardness of the tap water was tested several times and was found to be above 120 ppm. This is an acceptable range for flotation and therefore it was not adjusted.

The exact procedure that was used in the evaluation of the various formulations and in all subsequent trials is as follows. 100 grams (air dry) Kalamazoo gazette, a letterpress printed groundwood newsprint, was torn into approximately one inch squares. All inserts were removed from the newspapers. This stock and all the chemicals to be used were then added to 2500 ml of tap water at 45°C in a commercial size (1 gallon) Waring blender. It was then pulped at low speed for several minutes. After the pulping time had been completed the blender was shut off and the pulp allowed to soak, with the cover on, for the indicated period. The pulp was then added to the cell and 45°C tap water added until the cell consistency was 0.45%.

In order to avoid any variability in the pulping or holding time, each pulp produced only enough for one flotation run. If a large batch containing enough pulp for several floats had been used, the holding time would have been different for each.

The stock was floated for 12 minutes with the air flow at maxumum and the recirculation adjusted to get good flow in the cell, and 3/8 to 1/2 inch of foam. The foam was manually scraped off. See appendix 1 for flotation cell details.

After 12 minutes the stock was discharged into a large container and Buchner funnel pads were made on all the stock. Usually 8 to 10 pads per flotation run. If a smaller number of pads were made, the drainage time was too long and the formation was not acceptable, due to the larger amount of fiber in each pad. The smaller pads that were produced if the stock was divided into 8 to 10 pads were more uniform.

Table I lists the combinations that were tried in order to find a good formulation. Several of the formulations produced good results. All percentages listed are based on the air dry weight of fiber.

formulation	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
sodium silicate	0	5.0	5.0	5.0	6.3	3.5	5.0	5.0	5.0	5.0	5.0
oleic acid	0	0.6	0	0.6	0	0	2.0	2.0	1.5	0	0
stearic acid	0	0	0	0	0	0	0.25	0.25	0.25	0	0
CF-10	0	0	0	0.5	1.2	0.7	1.3	1.3	1.0	0	1.0
potassium soap	0	0	1.0	0	2.5	1.4	0	0	0	1.5	1.5
pulping time (minutes)	4	10	5	5	4	4	4	4	3	4	4
soaking time (minutes)	10	5	10	10	10	10	10	0	10	10	10
temperature °C	43	42	40	40	43	45	45	45	45	45	45
pH	8	8.5	8.5	8.5	8	8	8.5	8.5	8.5	8.5	8

TABLE I

Phase I de-inking formulations

note: all entries are percent chemical based on the air dry weight of fiber unless otherwise indicated.

All of the formulations were evaluated by using the El Repho brightness meter and by visual examination of the ink specs present in the sheet. Some formulations removed so much of the ink that it was difficult to discern any ink specs at all.

Once a formulation was chosen as the best one, it was then adopted as the standard formulation. It was then tested repeatably to insure that reproducible data was capable of being generated. Once the reproducibility was established, Phase II commenced. This is the study of the effect of pigments in the flotation de-inking of newsprint.

Phase II- Determination of the effect of pigments

The major difficulty that others have encountered in attempting to determine the effect of pigments in flotation de-inking is exactly what causes the brightness increase to occur, if in fact it does. As stated previously, Raimondo (40) did the most complete study and found that the addition of pigments definitely caused the brightness of the pulp to increase. However his study failed to accurately answer the question of why it increased. Although he did conclude that it was probably due to the inherent brightness of the pigment itself, his experimental design did not allow him to actually determine it with any degree of conclusiveness. Therefore the objective of Phase II was to make it possible to differentiate between 1) a brightness increase due to the inherent brightness of the pigment present in the sheet or 2) an increase in brightness due to an improvement in the operation of the flotation cell and the flotation mechanism. In order to do this the following procedure was established.

Two concentrations of pigment were added to the pulper coincidental with the addition of the chemicals and water. A low range of 5.3% (based on O.D. fiber) and a high range of 16.0%. The standard pulping and de-inking procedure were followed. Five runs were performed at each addition level. The brightness was then measured on the Buchner funnel pads using an El Repho brightness meter on filter number 8. It was standardized using a standard having a reflectance value of 78.5. The El Repho

was used because it has an integrating sphere and as such is not effected to any degree by the roughness of the surface being tested. The Buchner pads tended to have a very rough topside. The percent ash was measured (according to TAPPI standard T413 ts-66, Ash in paper). The next series of runs had the pigment added not in the pulper but immediately following flotation, just prior to the making of the pads. The amount added was based on the ash tests performed on the sheets that had the pigment added before flotation. The pigment was dispersed in water in the blender for a few seconds to disperse it and was then added to the pulp. As before 5 runs were performed on each level.

This procedure was designed to allow the determination of the cause of any brightness change that might occur. If the sheets with the pigment added before had a higher brightness than those which had the pigment added after flotation, then it can be assumed the pigment aided in the flotation and removal of the ink and impurities. If the results were the same then the brightness increase could be solely attributed to the inherent brightness of the pigment present. The pigments used were talc and diatomaceous earth which were listed in the literature as having been previously used for this purpose.

PRESENTATION AND DISCUSSION OF RESULTS

Phase I-Developement of the de-inking formulation

The results of the various formulations tried are listed in Table II.

TABLE II

Brightness results of Phase I formulations

formulation	BRIGHTNESS filterside	topside
I	32.7	33.8
II	34.9	34.8
III	39.2	37.6
IV	43.3	40.2
V	47.0	45.7
VI	45.5	46.3
VII	45.1	45.0
VIII	45.4	45.0
IX	41.9	45.9
X	42.9	43.8
XI	43.0	43.9

The first trial was performed without the addition of any chemicals. It was not anticipated that an extensive amount of ink would be removed and it was not, as the low brightness indicates. Surprisingly though, a good amount of foam was generated by the recirculation through the cell but the ink was not collected and floated out to any degree because there were no chemicals to act as collectors or foamers. As a result the foam was not very stable and the ink also clung to the walls of the cell. Also, since the flotation was not selective, a lot of fiber was floated out along with a very small amount of ink.

The percent yield was 87%.

The first chemical formulation, formulation II, was a simple one and generated more foam and removed a lot more ink than I, but still left a lot of ink in the pads. The amount of foam was still not enough and it was not very stable. In addition the problem of excessive amounts of ink clinging to the cell walls persisted.

In an attempt to improve the foaming another chemical was tried in trial III. This was potassium soap. It's a combination of 45% oleic acid, 5% stearic acid, and 50% distilled water. It was thought that this might perform better than the acid form, and it did improve foaming some. However it still did not remove the ink acceptably.

Formulation IV utilized another surfactant or dispersant type chemical, CF-10, in addition to sodium silicate and oleic acid. It's a product of Rhom and Haas. It did not change the foam generation a noticeable amount but did function to reduce the amount of ink clinging to the walls of the cell. As a result the ink was removed better and a brightness increase of several points was experienced.

The next trial, number V, used sodium silicate in combination with the potassium soap and CF-10. Very good foam generation occured and excellent ink removal. A few ink specs remained but the overall appearance was very good.

Formulation VI used the same chemicals as V, but the concentrations were reduced by one-half in order to see if these

lower concentrations would perform acceptabley. The amount of foam was reduced but there was still a fair amount. Most of the ink was removed but there were more ink specs present in the sheet than in V, and as a result the overall appearance was not as good.

Run VII was a combination of oleic and stearic acid, and the prepared potassium soap was not used. Sodium silicate and CF-10 were also used. The result was excellent foam generation and excellent ink removal. The foam was very stable. There were hardly any ink specs present in the sheet and its overall appearance was the best of any trial.

In order to investigate the possibility of reducing the pulping time, trial VIII consisted of the same chemicals as VII and in the same percentages. In this case however, there was no soaking time. Following the pulping the stock was transferred immediately to the flotation cell. As expected the foam generation was the same, and the brightness was close to that of VII. However there were a noticeable amount of ink specs present in the sheet which were not there in run VII. Thus the additional 10 minutes soaking time seems to allow better reaction of the chemicals with the ink and fiber and improve the ink removal.

In trial IX the oleic and CF-10 concentration were reduced slightly and the pulping time cut to 3 minutes. The foam generation was still good but a little more ink remained in the sheet as a result of the reduced mechanical action and reduced

chemical concentration.

Trial X was an attempt to see if trial III might perform better if the amount of potassium soap were increased. This combination still did not generate as much foam as several others and the ink removal was subsequently not as good.

Trial XI was the same as X except that CF-10 was also added. Its overall appearance was just slightly better than X.

Most of the work done in this part of the laboratory work dealt with changing the chemicals and their concentrations. However work was also done in finding a good pulping and soaking time combination. This is one area that varies a great deal industrially and the total soaking and pulping times sometimes approach 3 hours. However this experiment used letterpress printed newspapers and there were not any difficult to remove impurities such as adhesives present. Therefore such a lengthy period was not thought necessary.

As a result, the initial pulping time was set at 10 minutes. It was found however that 4 minutes was sufficient and this was adopted as the standard. The soaking time, which in the literature was mentioned as being up to two and a half hours, was set at 10 minutes. This provided a long enough time for the chemicals and heat to react with the fibers and ink. In both the case of pulping time and soaking time, a more optimal time could probably be found. However the total of 14 minutes for both produced very good results. A very lengthy time might have resulted in a slightly higher brightness. It was found

expedient however to keep this time down to a minimum.

The temperature and pH for de-inking this type of stock were well defined in the literature and were not varied. A temperature of 45°C and a pH of 8-8.5 was used in all cases. The pH did not vary much from the start of the pulping to the end of flotation. The temperature was constant until the stock was removed from the cell. While sitting in the container prior to the making of pads the temperature dropped some, but did not fall below 40 C.

The results show that formulations V, VI, VII, and VIII all produced good brightness sheets. (see Table II) Formulation VII was chosen as the standard based on several factors. It gave the most stable foam of all the formulations, and the froth it produced was very concentrated with ink. The amount of ink specs present in the pads based upon visual examination was the least of all the formulations. Thus VII produced the sheet with the best overall appearance.

It must be mentioned that the formulations used, and the one chosen as the standard, are not optimal ones. The percentages of chemicals used and the thermal and mechanical inputs could most likely be improved upon if more work was done. However the objective of Phase I, which was to develop a suitable de-inking formulation, was realized. The following was designated as the standard formulation: 5.0% sodium silicate, 2.0% oleic acid, 1.3% CF-10, 0.25% stearic acid, 4 minute pulping time, 10 minute soaking time, 12 minute flotation time, ph=8-8.5,

and a temperature of 45°C.

An important point that must be considered is that the experimental procedure must be capable of generating reproducible results. If it is not, then it will be impossible to draw any valid conclusions from the data.

In order to insure that data is reproducible, 10 repitions or in other words 10 separate flotation runs were performed with all parameters held constant. The objective was to produce consistent results.

As Graph 1 shows, the procedure was acceptable and the results were consistent. The average topside brightness was 50.3 with a standard deviation equal to 0.51. The filterside had a brightness of 48.1 with a standard deviation of 1.8. Again the filterside had a lower brightness because the suction of the Buchner funnel apparatus caused the ink to concentrate on the suction or filterside. Since the ink was not as uniformly distributed on the filterside but tended to be non-uniform the standard deviation was lower on this side. The non-uniform distribution of ink can be attributed to varying amounts of suction on the bottom side. There was less suction at the very edges of the pad and in the very center. The remainder of the bottom surface had slightly more suction so that the ink deposited here to a larger degree. In addition, the drainage rate of the stock sometimes varied and this may have lead to different amounts of ink in different areas.

Now that the experimental procedure had been shown to be capable of producing consistent results from run to run, the

study of the effect of pigments in the cell could be implemented.

The average yield following flotation was 94-96%, or in other words a loss of 4-6% of fiber in the froth. This is higher than most industrial operations. One reason is that no fiber was lost during the dewatering of the stock, i.e. while making pads. In an an industrial operation the methods used to thicken the stock cause more fiber to be lost than this.

Phase II-Determination of the effect of pigments

The addition of pigments in flotation de-inking is postulated to aid in the flotation and removal of ink and impurities. Phase II was designed to investigate the effect of adding two different pigments, talc and diatomaceous earth. These pigments were chosen because they have been used for this purpose before.

Talc was the first of the two pigments studied. The final results however, were the opposite of what was anticipated.

It did function well to collect and absorb the ink onto its surface. The surface of all the talc was heavily concentrated with ink and a majority of the talc floated and was removed. In the 5.3% pigment addition level, an ash content of 1.4% was measured, and in the 16.0% level the ash was 3.2%. Thus in both cases, a majority of the pigment was removed. However the pigment that remained in the sheets after flotation was so concentrated with ink that the brightness of the pads were decreased. (see Graph 1)

The low pigment range had a brightness of 48.4 topside

and 45.1 filterside. The higher pigment addition level had a topside brightness of 48.1 and the filterside decreased to 43.7. The lower brightness of the filterside in both cases can again be attributed to a concentration of the ink and pigment at this side, which was caused by the suction of the Buchner funnel.

Talc is a hydrophobic and organophilic pigment that exhibits a slightly positive surface charge (51). The organophilic properties resulted in the ink attracting to the talc readily. The talc was also removed to a great extent by flotation due to its positive surface charge. This reacted well with oleic and stearic acid which are both anionic collectors. Since this pigment did not increase the brightness, a pigment with slightly different properties was chosen for the next series of runs. Diatomaceous earth is a more hydrophillic pigment and it was believed that it might react differently.

The more hydrophilic properties of the diatomaceous earth was immediately apparent upon addition to the blender. Whereas the talc floated on top of the surface as a mass upon addition, the diatomaceous earth immediately sank and dispersed in the water.

The procedure was identical to that for the talc. A low range of 5.3% and a high range of 16.0% of diatomaceous earth was added to the pulper. This pigment performed as postulated and caused a noticeable brightness increase. (see Graph 2) The low range resulted in a pulp having a topside brightness of 52.8 and a filterside of 53.0. The high range had values of 53.7 and 57.3 respectively.

The higher brightness of the filterside, especially in the high pigment addition level, was again attributed to a concentration of pigment at the suction side. These sheets were then tested to determine the amount of pigment that actually remained in the sheet after flotation. The low range showed a percent ash of 5.13% and the high range 13.41%. Thus a majority of the pigment was not floated out as it was in the case of the talc. In addition the pigment appeared very white in the sheet and it was not contaminated with ink like the talc.

The next step was to add the diatomaceous earth after the flotation cell. The amount to add was based on the amount actually present in the sheets following flotation, as determined by the percent ash. Thus 5.13% and 13.41% diatomaceous earth, based on the O.D. weight of fiber, were added to the stock after the flotation cell. The pigment was first slurried in the blender for a few seconds and then added to the stock.

The brightness values measured for the stock having pigment added after flotation were 52.30 topside and 53.2 filterside for the low range of addition, and 52.3 topside and 57.1 filterside for the high range. (see Table 3)

As Graph 2 shows, if the brightness values for the addition of pigment before flotation are compared to that of after flotation it can be seen that the values are very close at both low and high addition levels.

Table 3 shows this data and the standard deviations associated with each. By using a range of plus or minus two standard

deviations around the mean the indicated ranges can be obtained. This range will include 95% of the data, or in other words a 95% confidence limit. By comparing the topside values before to the topside values with the pigment added after flotation, it can be seen that the ranges overlap considerably. The same is true for the filterside. Thus it can be concluded with a high probability that this data for the addition before and after flotation is not significantly different. Even though the means are not the same the two groups of data can be said to be the same statistically.

Conclusions

The addition of diatomaceous earth to the flotation cell, under the confines of this experimental procedure, made no discernible difference in the appearance or brightness of the deinked stock. The talc actually decreased the brightness. Thus although previous studies (40) by other authors have theorized that the addition of pigment improved flotation and ink removal this was shown not to be the case. The addition of talc or diatomaceous earth in order to increase brightness was shown not to be justified.

Recommendations

Although the results indicate the pigments do not aid flotation, it seems possible that more work could be done in this area.

Other pigments could be examined. The talc acted very well in attracting to the ink and if the small amount of talc remaining in the sheet was removed it may aid in brightness developement. Other collectors, such as cationic collectors, might be tried. One of these collectors might possibly remove the talc and/or diatomaceous earth better.

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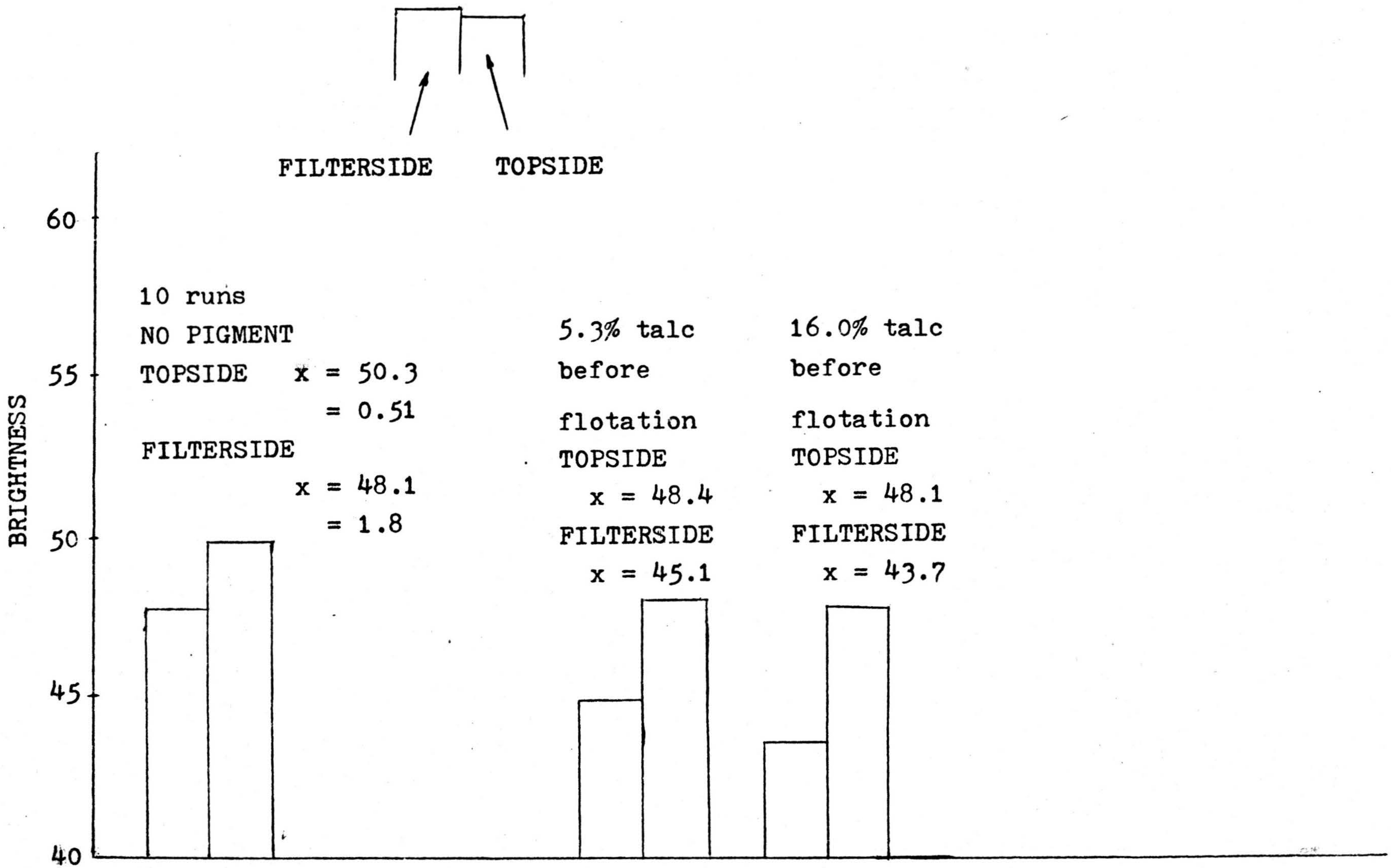
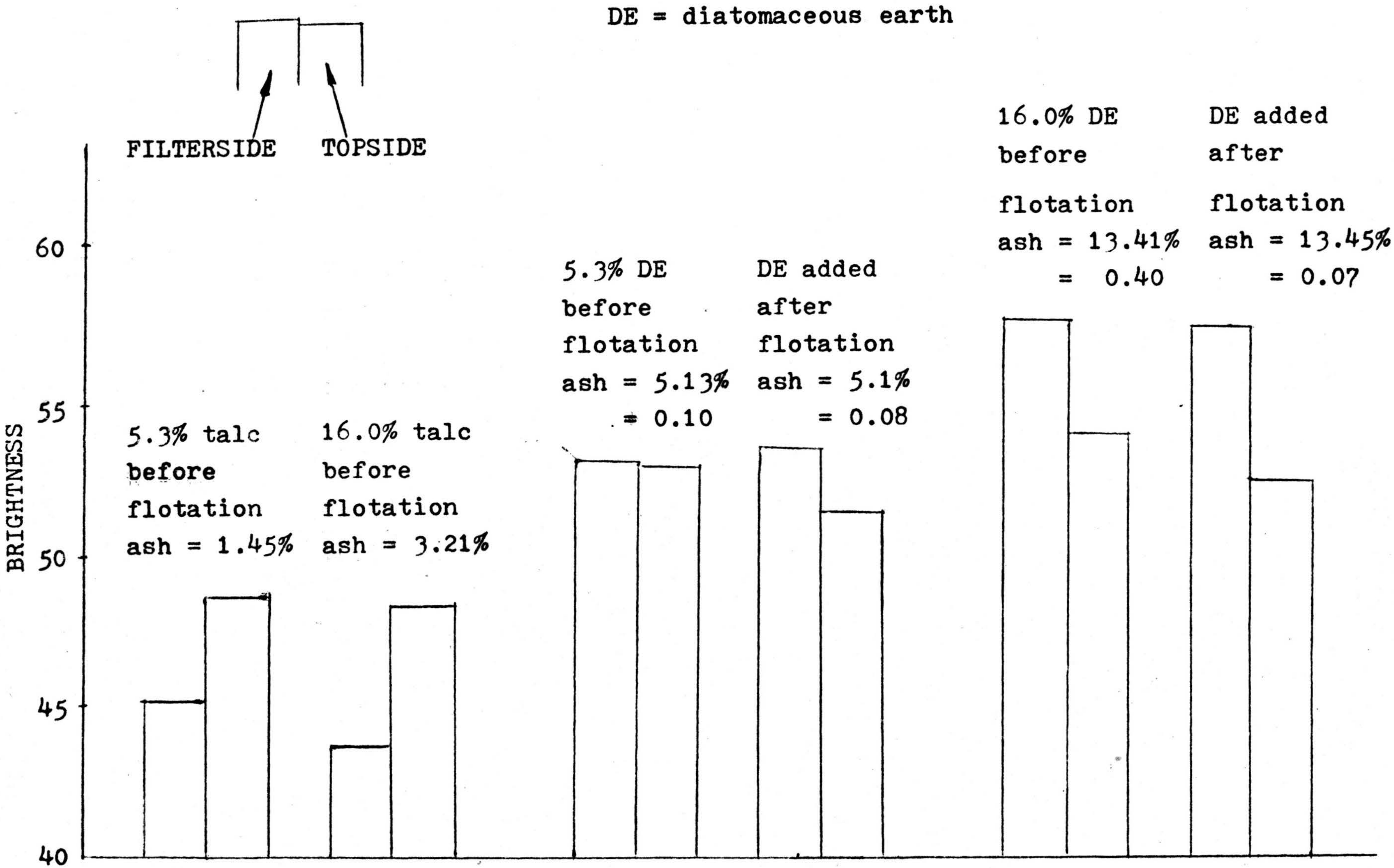


GRAPH 1

Brightness before and after talc addition



GRAPH 2

Effect of pigment addition on brightness

	5 runs 5.3% DE before flotation	5 runs DE added after flotation	5 runs 16.0% DE before flotation	5 runs DE added after flotation
TOPSIDE	x = 52.8	x = 51.2	x = 53.7	x = 52.2
	σ = 1.63	σ = 1.1	σ = 1.09	σ = 1.05
	49.5 - 56.1 [a]	49.0 - 53.4	51.5 - 55.9	50.1 - 54.3
FILTERSIDE	x = 53.0	x = 53.2	x = 57.3	x = 57.1
	σ = 1.88	σ = 0.50	σ = 1.58	σ = 0.59
	49.2 - 56.8	52.2 - 54.2	54.1 - 60.5	55.9 - 58.3

TABLE III

Brightness data for the addition of diatomaceous earth

a = mean plus or minus two standard deviations

σ = standard deviation

Appendix 1 - Flotation cell details

The flotation cell used was a Voith laboratory cell. It consists of a wquare tank of plexiglass plates. The plexiglass cell and a steel welded motor spider are mounted on a common sectional steel baseplate. The rating of the 3-phase A.C. motor is 0.18 KW, its speed 1500 rpm. The propeller coupled with the shaft runs at the same speed. Installed in the pipe which connects the suspension outlet opening in the cell with the spiral case ahead of the propeller is a one inch I.D. valve which permits control of the stock in circulation. A discharge pipe enables the stock to be removed. The flow conditions ahead of the froth discharge channel can be controlled with the aid of the valve which can be adjusted in height. The air flow is controlled by a valve. The air is directed concentrically through a separate air pipe into the space below the propeller and mixed with the suspension discharging from the spiral case. To prevent the entrainment of infiltrated air the one inch I.D. stock regulating valve should be adjusted so that a level of about 10 mm is maintained in the overflow compartment of the flotation cell.