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## An Evaluation of Phosphates as Dispersing Agents in the Deinking of Catalogue Wastepaper by Flotation

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AN EVALUATION OF PHOSPHATES  
AS DISPERSING AGENTS IN THE  
DEINKING OF CATALOGUE WASTEPAPER  
BY FLOTATION\

Leif Christensen  
1962-63 Senior Thesis

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Leif Christensen  
Department of Paper Technology  
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"AN EVALUATION OF PHOSPHATES  
AS DISPERSING AGENTS IN THE  
DEINKING OF CATALOGUE  
WASTEPAPER BY FLOTATION"

Abstract:

Employing a Wemco three liter laboratory flotation cell and using the dispersing agent as the independent variable erratic trends suggested that trisodium phosphate and tetrasodium pyrophosphate increase the brightness gain in froth flotation deinking and that trisodium phosphate promotes higher brightness gains than tetrasodium pyrophosphate in concentrations ranging from 0.02 to 0.2 percent, (based on oven dry wastepaper). Conclusions could not be drawn for other salts evaluated and also are definitely not decisive for the two salts described. With a material like wastepaper it is difficult, even with the best endeavor to composit the sample, to obtain a large number of specimens, each of which is truly representative of the composite. It would have been desirable if time had been available, to have worked with a much more extensive experimental procedure.

Objective:

Phosphate salts are often employed as dispersing agents in flotation deinking. The literature does not contain empirical evaluations of these salts relating the final deinked brightness as a function of salt concentration. It is the objective of this work therefore to evaluate tetrasodium pyrophosphate and trisodium phosphate as dispersing agents in flotation deinking.

Literature Survey:

Although froth flotation is not unique in the mining industry where it is used for concentrating low grade ore it is a relatively new practice, but not idea, in the paper industry for deinking waste paper. In both industries dispersions are placed in a vat along with chemicals, and bubbles carry part of the dispersion to the surface where it is removed. The difference between ore and waste paper flotation is that in the mining industry the desired ores are carried to the surface while in the paper industry the undesired ink is carried to the surface. Both operate on the principles of surface differences where the desired ore is more strongly attracted to the bubbles in the mining industry and where the ink is more strongly attracted to the bubbles in the paper industry.

In froth flotation for deinking waste paper it is desired to dissolve the ink binder, separate, disperse, keep dispersed the ink and fiber, collect the ink but not the fiber on air bubbles, float the ink to the top of the flotation cell and skim the ink froth from the flotation cell leaving clean fiber which may be drawn off the bottom.

The first step in dispersing the ink and fiber is dissolving the binder which holds the ink to the fiber. An ink may be defined as a fine dispersion containing dyes and coloring agents, vehicles which may consist of drying oils, non-drying oils and volatile solvents, resins, driers and modifiers.<sup>1</sup>

Ink is generally about  $\frac{1}{2}$  to 2 percent of the weight of the paper, and this must be completely removed if deinked pulp is to be produced. From the standpoint of ease of deinking, there are three principal types of inks.<sup>2</sup>

1. Drying, oil-base inks.
2. Non-drying, oil-base inks.
3. Inks having a synthetic resin base.

Drying, oil-base inks which are slightly oxidized can be readily sponified by alkali. However, completely oxidized oil-base inks, non-drying, oil-base inks, and inks having a synthetic resin base cannot be completely sponified by alkali of ordinary concentration, and consequently special methods of deinking must be used for papers containing these inks. The various high-gloss inks are extremely difficult, if not impossible, to remove with alkali. The trouble is increased if polyethylene is used as a compounding agent in the ink. Solvents (e.g., tri- or tetrachloroethylene, benzene or carbon tetrachloride) or soaps and detergents can be used to aid in the deinking of these papers.

Deinking processes have a common factor in that the stock must be properly prepared for deinking. Preparation is complete when the ink is completely removed from the fiber and separated into particles of proper size so it may be removed from the slurry by the particular deinking process under consideration. Preparation of waste paper for deinking can be looked at from two vantage points, proper mechanical treatment and proper chemical treatment.

Proper chemical treatment utilizes alkali and dispersing agents. Alkali, a common sponifier,<sup>3</sup> is used in the deinking formula for two purposes.<sup>4</sup>

1. To remove rosin sizing from the paper.
2. To sponify the ink vehicle and release the pigment in the ink.

Sodium carbonate and sodium hydroxide are two common deinking alkali. Sodium carbonate is a milder agent than sodium hydroxide and would be preferable when the waste paper has a high groundwood content which is very susceptible to chemical shrinkage and cannot tolerate extensive alpha cellulose destruction. It also yields better pH control. The sodium hydroxide is preferable when deinking chemical pulps which contain difficult inks, about 5 percent sodium hydroxide is the maximum used.

Sodium silicate is another deinking sponifying agent and its use can, but not always, produce a brighter pulp than alkali.<sup>5</sup> This increase in brightness can be attributed to its greater surface activity which can result in better sponification of the ink binder and better dispersion of the ink. Sodium silicate is also effective at a lower pH than alkali and does not have the tendency to yellow groundwood. A ratio of 1 part  $\text{Na}_2\text{O}$  to 1.6 parts  $\text{SiO}_2$  is considered best for deinking.

Detergents are also used in the deinking process to aid in loosening the ink from the paper. They are attributed to have the following properties.<sup>6</sup>

1. Excellent compatability with anionics and cationics (they do not form insoluble metal salts).



2. The ether linkage insures excellent stability in either acid or alkali mediums. They also show stability with oxidizing agents such as peroxide, hypochlorite and perborate.
3. They demonstrate good heat stability which is an important factor under many conditions.

In deinking ordinary rosin-sized papers, the alkali reacts with the rosin size to form rosin soap, which acts as a detergent for the ink particles.<sup>7</sup> In such instances when detergent is formed with the alkali the addition of more detergent may become unnecessary.

The second phase of deinking stock preparation is proper mechanical treatment which can occur simultaneously with addition of the before mentioned chemicals as well as with the dispersing agent which follows in this discussion. While chemicals are used to loosen ink from the fiber mechanical treatment yields physical attrition whereby the ink and fiber are separated and thoroughly dispersed. An excellent power impact to insure the thorough dispersion desired runs, in the approximate range of 10 horsepower-days, per ton of pulp. Throughout the waste paper deinking preparation temperatures ranging from 120 to 200° F. are employed.

After the ink and fiber are in dispersion the ink must not extensively agglomerate and must not redeposit on the fiber. For this purpose dispersing agents are used and included as part of the pulping chemical formula. The previously mentioned alkali has these dispersing properties and much wash type deinking is done with just plain alkali,<sup>8</sup> however, additional dispersing agents are often used. To understand

the application of dispersing agents in flotation deinking the nature of the fiber and ink dispersion must first be considered.

Cellulose fibers absorb hydroxyl ions from water, setting a layer of negative charges adjacent to the fiber. Positively charged ions are attracted, thus setting up a potential across the layer from the fiber surface to the outer reaches of the positive ions.<sup>9</sup>

A similar system occurs with clay particles<sup>10</sup> and therefore with an ink suspension.

The tendency of cellulose or ink to surround itself with positive ions attracted to the negative surface is partially overcome by the thermal motions of the positive ions creating a diffuse ionic layer around the particle known as the zeta potential. By placing an ionizing salt in an ink slurry the positive metal ions of the salt will set up this zeta potential to a greater or lesser extent, giving the particles in the system a positive charge of greater probable magnitude than the former negative charge and also aid in preventing the ink and cellulose from either agglomerating individually or mutually.

The salt employed as a dispersing agent can have a marked effect upon the zeta potential of cellulose. In a study of the effect of monovalent, divalent and trivalent metallic chlorides a marked change in the zeta potential occurred<sup>11</sup> with different salts.

Phosphate salts are common dispersing agents in flotation deinking. The industrially important sodium phosphates may be classified:<sup>12</sup>

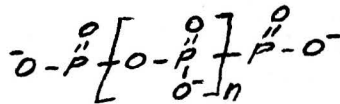
Alkali metal metaphosphates, such as  $\text{NaPO}_3$ , sodium meta phosphates, and sodium hexametaphosphate,  $(\text{NaPO}_3)_n$ , or Graham's salt.

Alkali metal polyphosphates, such as  $\text{Na}_5\text{P}_3\text{O}_{10}$ , sodium tripolyphosphate.

Alkali metal pyrophosphates, such as  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ , sodium or tetrasodium pyrophosphate.

Alkali metal orthophosphates, such as  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ .

These phosphate compounds are inorganic polymers.<sup>13</sup>



If the dispersing action is related to the metal ion cloud concentration surrounding the ink and fibers in suspension, tetrasodium pyrophosphate should be a more effective dispersing agent with 20.6 percent sodium as compared to trisodium phosphate which contains 18.7 percent sodium.

Deinking wet strength papers with special inks may possibly be accomplished more effectively in an acid medium rather than a basic medium and based upon reference 11 aluminum chloride could be an effective dispersing agent in such acid situations.

After the ink binder has been removed and the ink and fiber have been dispersed the ink is passed into a flotation system where bubbles are formed which carry the ink to the surface where it may be skimmed. Here basically two types of chemicals are employed, frothers whose specific purpose is to create bubbles, and collectors which aid in attaching the ink particles to the bubbles for their ride to the top of the flotation cell.

Frothers are slightly ionizing chemicals consisting of a carbon hydrogen chain and one hydroxyl group. Typical frothers are higher alcohols, phenols, and other materials fulfilling the specifications just described. The frother must create bubbles which will remain free and essentially the same size as when they are generated.<sup>14</sup> The bubbles must also be sturdy. The frother has to be nearly, but not quite, insoluble, and slightly ionizing. This type of chemical will form a fuzz around the bubble, or interface, consisting of the long chain portion of the frother molecule<sup>15</sup> orientated toward the center of the bubble. This establishes a charge around the bubbles and has the effect of making them repel each other and thus establishing the required stable bubbles. In industrial practice pine oil or one of the higher alcohols is generally used as the frother.<sup>16</sup>

The mechanism of bubbles is usually attributed to their hydrophobic end pointing toward the center of the bubble and their hydrophilic end extending out in desire of water.

Collectors are used in conjunction with frothers and are specific chemical compounds used to collect the ink particles on the surface of the bubble. Collectors are usually highly water repellent materials such as fatty acids, hydrocarbon oils, and a long list of other materials.<sup>17</sup> Oleic acid and stearic acid are two specific collectors.<sup>18</sup>

Activators, depressants, and modifiers are applied to alter the basic characteristics of the frothers and collectors just described.<sup>19</sup>

In actual flotation, consistencies between 0.75 and 1 percent are usually used. Stock passes through a series of primary and secondary cells in parallel, totaling approximately eight in number. Rejects from primary cells are sewerred and rejects from secondary cells are returned to the primary cells. Tertiary cells can also be used. Frothers and collectors are applied continuously to the cells. The basic mechanism of practical flotation consists of forming the stable bubbles as previously described in this discussion and then adding a collector. A common collector is kerosene or fuel oil. The collector is hydrophobic and tends to coat carbon black and other coloring matter in the stock slurry. This then makes the coloring material also hydrophobic and in this water hateing condition it migrates to the inside of bubbles passing up through the solution. The coloring matter migrates into the inside of bubbles because the nature of the frother makes the inside or air side of the bubble water hateing and the hydrophobic coloring matter is more compatable in this location.

Studies of ink removed in flotation<sup>20</sup> reveal that particles of less than two microns display erratic behavior but generally stay in the stock slurry, particles from two to ten microns are removed and particles greater than twenty-five microns are not removed.

In matter of speculation if enough of the proper chemical and mechanical action were applied to the waste paper nearly all of the coloring matter could be removed from the fiber and reduced in particle size not to exceed

ten microns. After a series of initial flotation cells in which nearly all ink particles from two-ten microns would be removed, a specific flocculating agent could be applied to the system which would precipitate<sup>sp</sup> those ink particles of less than two microns upon one another to increase their size to the two to ten micron range making them susceptible to flotation. Such a system would probably involve the use of additional flotation cells which would be offset by a more thorough ink removal.

A new concept in deinking applicable to flotation is the application of an electrical potential across a stock slurry.<sup>21</sup> At present there are no apparent industrial applications of such a system.

Literature Cited:

- <sup>1</sup>Dr. Robert A. Diehm, Professor of Paper Technology, Western Michigan University; Kalamazoo, Michigan. Lecture on October 9, 1962.
- <sup>2</sup>Casey, Pulp and Paper, Volume I, page 383, Interscience Publishers, Inc., New York, 1960.
- <sup>3</sup>Felton, A.J., Deinking - Present and Future, Tappi 43, number 8, pages 193-200A, August 1960. A.B.I.P.C. 31:540.
- <sup>4</sup>Ibid., 2, p. 383.
- <sup>5</sup>Ibid., 2, p. 383.
- <sup>6</sup>Barker, Ernest F., "New dry process intrigues deinkers" Paper Trade Journal 143, number 43, pages 28-34, October 26, 1959 A.B.I.P.C. 30:807.
- <sup>7</sup>Ibid., 2, p. 384.
- <sup>8</sup>Ibid., 2, p. 382.
- <sup>9</sup>Ibid., 2, p. 15.
- <sup>10</sup>Besdell, Bernard K., "The Rheological Properties of Clay-Water Suspensions"; Paper Mill News, June 6, 1948.
- <sup>11</sup>Briggs, D.R., Journal of Physical Chemistry, Volume 32, pages 641-646, 1928.
- <sup>12</sup>Shreve, Morris R., The Chemical Process Industries, Second Edition, McGraw-Hill Book Company, Inc., New York, 1956.
- <sup>13</sup>Chaberek, Stanley and Martell, Arthur E., Organic Sequestering Agents, Copywrite 1959, John Wiley and Sons, Inc., New York.
- <sup>14</sup>Jelks, J.W., Deinking by the Flotation Process, Tappi 37, number 1, pages 149-50A, January, 1954. A.B.I.P.C. 24:441.
- <sup>15</sup>Jelks, J.W., Developments in Flotation Deinking of Waste Paper, Tappi 37, number 10, pages 176-80A, October 1954, A.B.I.P.C. 25:190.
- <sup>16</sup>Ibid., 15
- <sup>17</sup>Ibid., 15
- <sup>18</sup>Ibid., 15

<sup>19</sup>Jelks, J.W., "Flotation Opens New Horizons in the Paper Industry," Paper Trade Journal 134, number 17, pages 22,24 and 26. April 25, 1952, A.B.I.P.C. 22:663.

<sup>20</sup>Heinz, Mark, "Deinking by Flotation," Seventh Deinking Conference.

<sup>21</sup>United States Patent 2,743,178, Krodel, W.J., Process for De-inking Printed Waste Paper, August 24, 1956. Filed July 19, 1948. 2 claims.



Procedure:

Handsheet formation and testing:

1. Two liters of distilled water were heated to 60°C. in a Tappi standard disintegrator.
2. Twenty-seven grams air dry pulp, 0.46 percent sodium carbonate (based on oven dry pulp), and 0.20 milliliters of water per 100 grams of oven dry paper , were added to the disintegrator and it was run for 2000 revolutions.
3. 148 milliliters of the disintegrated stock were separated and filtered in a 12 centimeter buchner funnel for an original brightness pad.
4. The remaining stock was added to the laboratory flotation cell along with an additional liter of distilled water, 0.1 milliliters of kerosene, 0.1 milliliters of pine oil and 0.047 milliliters of Triton X-100 (a detergent). Initial consistency of flotation was 0.75 percent.
5. With maximum air passing through the flotation cell, flotation proceeded until no froth came over the lip, the cell was again filled to the lip with consequent washing of ink and froth back into the cell.
6. When no further froth came over the lip of the cell the stock was used to form a Noble and Wood handsheet, for final deinked brightness, which was pressed on the Noble and Wood press but not dried on the Noble and Wood Drier.
7. Both the original and final brightness handsheets were dried at constant temperature and humidity.

8. Ten brightness readings were taken on the bottom of the final brightness, Noble and Wood, handsheet and ten brightness readings were taken on the top of the initial brightness handsheet after the filter paper had been peeled away.

Comments:

9. The waste paper used was classified as #2 printed clippings and it was thoroughly mixed in a barrel before any laboratory work was attempted; the paper appeared like old catalogues. Each sample for pulping and flotation was selected in random increments from the barrel.

10. Two and sometimes three deinking operations were performed for each brightness value found in the statement of results.

Statement of Results:

Tetrasodium pyrophosphate as the independent variable: \*

% Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ·10H <sub>2</sub> O	Final G.E. Brightness	Original G.E. Brightness	Brightness I.P.C. Points	Gain % Gain
0.000	58.37	51.90	7.47	14.7
0.019	58.07	52.62	5.77	11.0
0.037	59.43	52.70	7.34	13.9
0.046	59.15	51.35	7.80	15.2
0.056	58.33	50.64	6.83	13.5
0.074	57.78	49.90	6.53	13.1
0.093	58.33	51.26	7.14	13.9
0.186	58.58	51.37	7.21	14.0
0.371	58.70	52.60	7.44	14.1
0.555	59.50	52.77	7.45	14.1
0.741	59.17	51.46	7.71	15.0
0.924	59.45	52.07	7.38	14.1

\*Brightness values are the average of two or more samples.

Statement of results con't.

Trisodium phosphate as the independent variable: \*

$\% \text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	Final G.E. Brightness	Original G.E. Brightness	Brightness I.P.C. points	Gain $\% \text{ Gain}$
0.000	58.37	50.90	7.47	14.7
0.019	59.12	51.37	7.75	14.4
0.037	59.22	50.88	8.34	16.4
0.056	59.98	51.42	7.56	14.7
0.074	59.33	50.66	8.67	17.1
0.093	59.32	49.95	8.37	16.8
0.186	60.05	50.79	9.08	17.9

\*Brightness values are the average of two samples.

Discussion of Results:

In gathering laboratory data dry wastepaper was used for each deinking run and a preflotation brightness handsheet was formed. It was believed that by using extreme caution in selecting uniform stock to deink, the preflotation brightness would be fairly constant and any fluxions in ink content would leave a somewhat proportional amount of ink in the deinked paper as well as be compensated by making many individual deinking operations. A large slurry of preflotation stock was not prepared because of the quantity which would be necessary to encompass the total dispersing agent evaluation and because of fear that the slurry would change upon aging. The idea of a large stock slurry from which constant stock could be used for all flotation runs may have been a better technique.

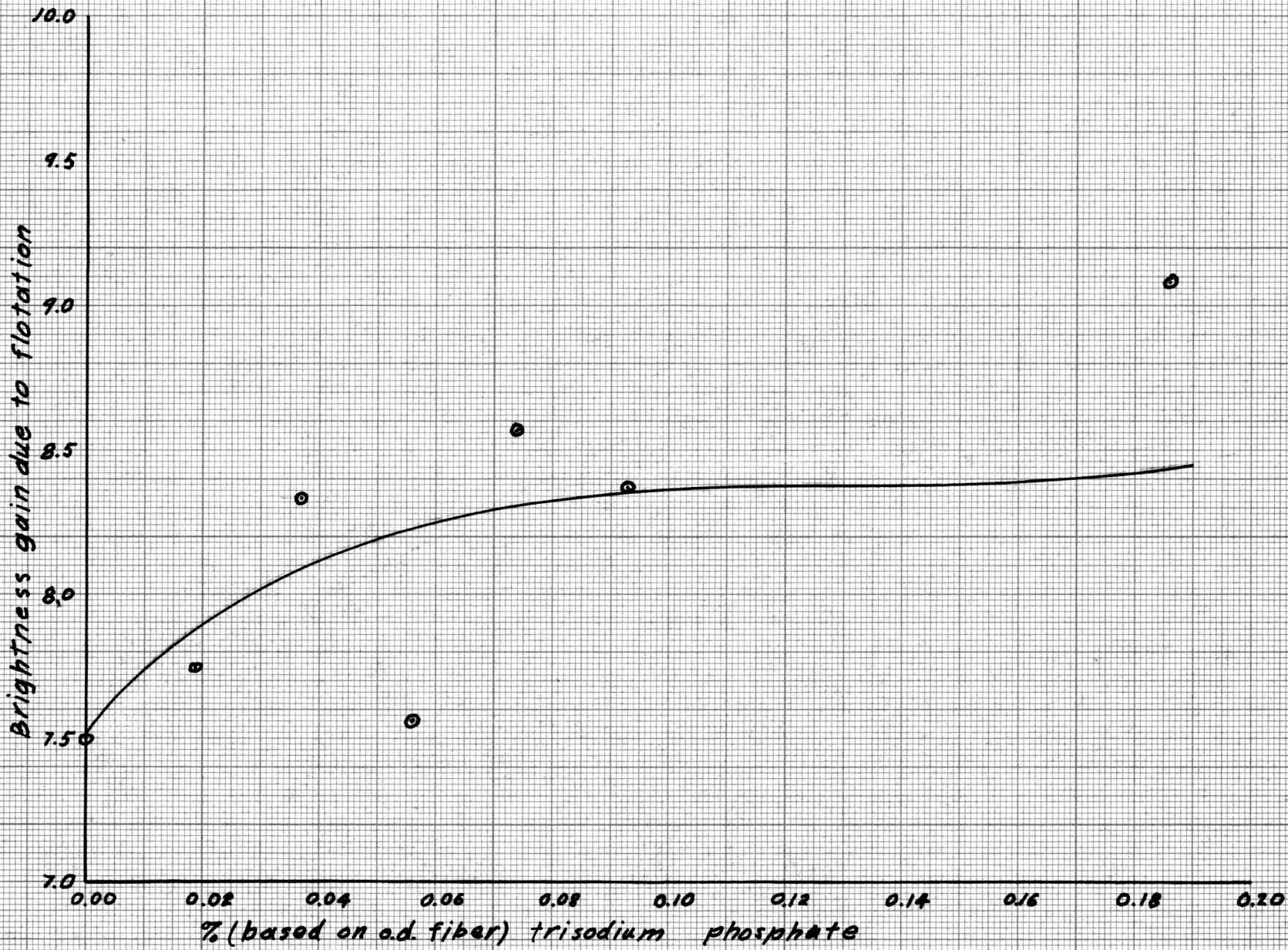
Deinked brightness handsheets were prepared on a Noble and Wood handsheet formation, although no additional water was employed, was the washing resulting in the handsheet formation. This technique was used however, because of the high filler content in the wastepaper which prolonged filtering a handsheet on a Buchner funnel into many hours.

Ten G.E. brightness readings were taken for each handsheet made and the average was taken as the brightness of the handsheet. Individual brightness values on a given handsheet ranged approximately  $\pm 1.5$  G.E. brightness points around the average value.

Discussion of results con't.

Graphical analysis shows the dispersing agents studied probably have a positive effect upon flotation deinking efficiency with the probability of trisodium phosphate promoting higher brightness gains in concentrations ranging from 0.02 to 0.2 percent (based on oven dry waste paper).

Graph I demonstrates the effect of trisodium phosphate upon the G.E. brightness increase and Graph II demonstrates the same relationship for tetrasodium pyrophosphate.







Discussions of results con't.

Graph III represents the effect of varying concentrations of trisodium phosphate upon the G.E. brightness before and after flotation while Graph IV does the same for tetrasodium pyrophosphate.

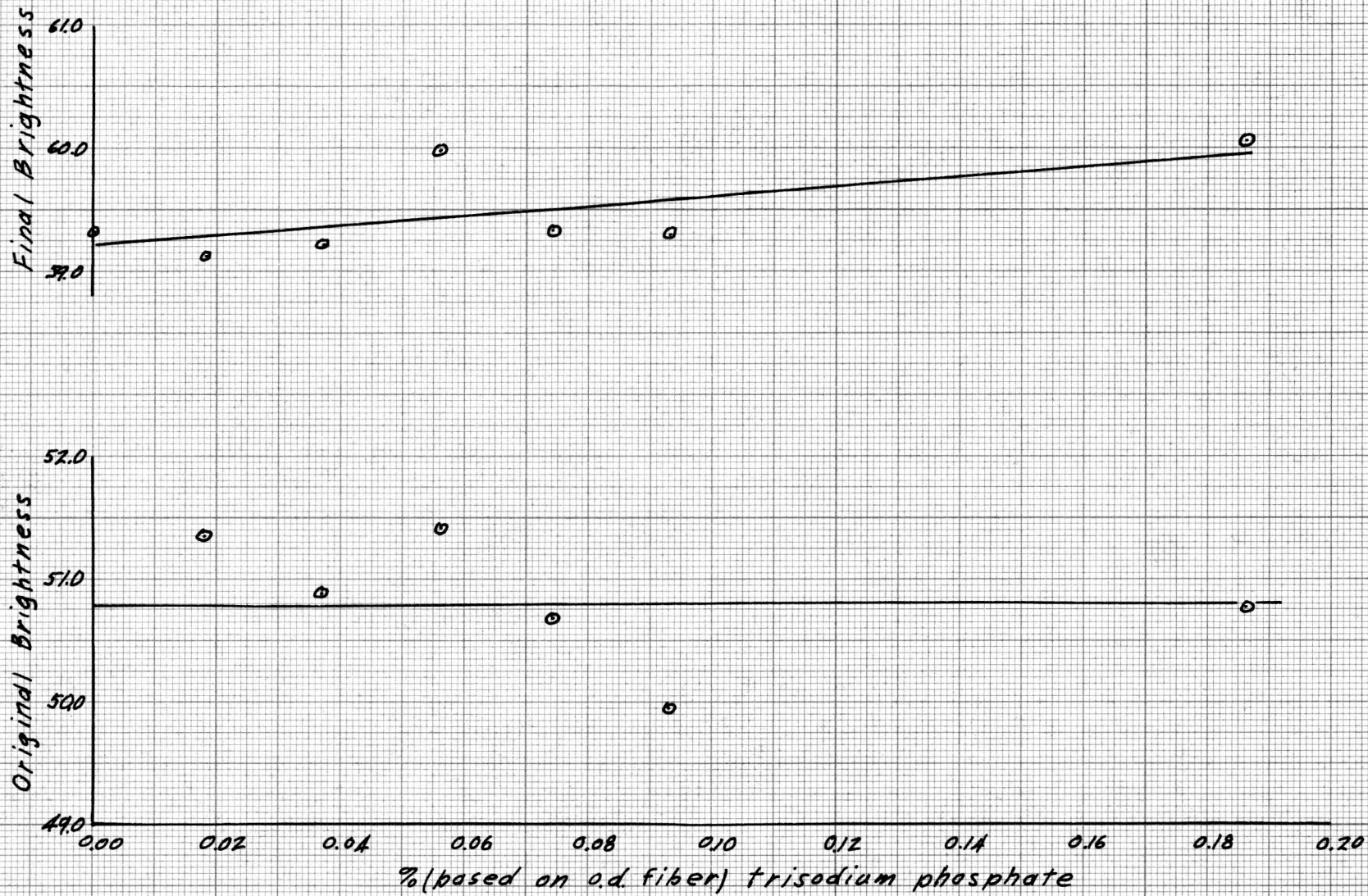
In actual operation of the laboratory flotation cell many variables could not be held constant. The most significant of these uncontrolled variables was the initial flotation stock which can account for a great deal of the erratic data.

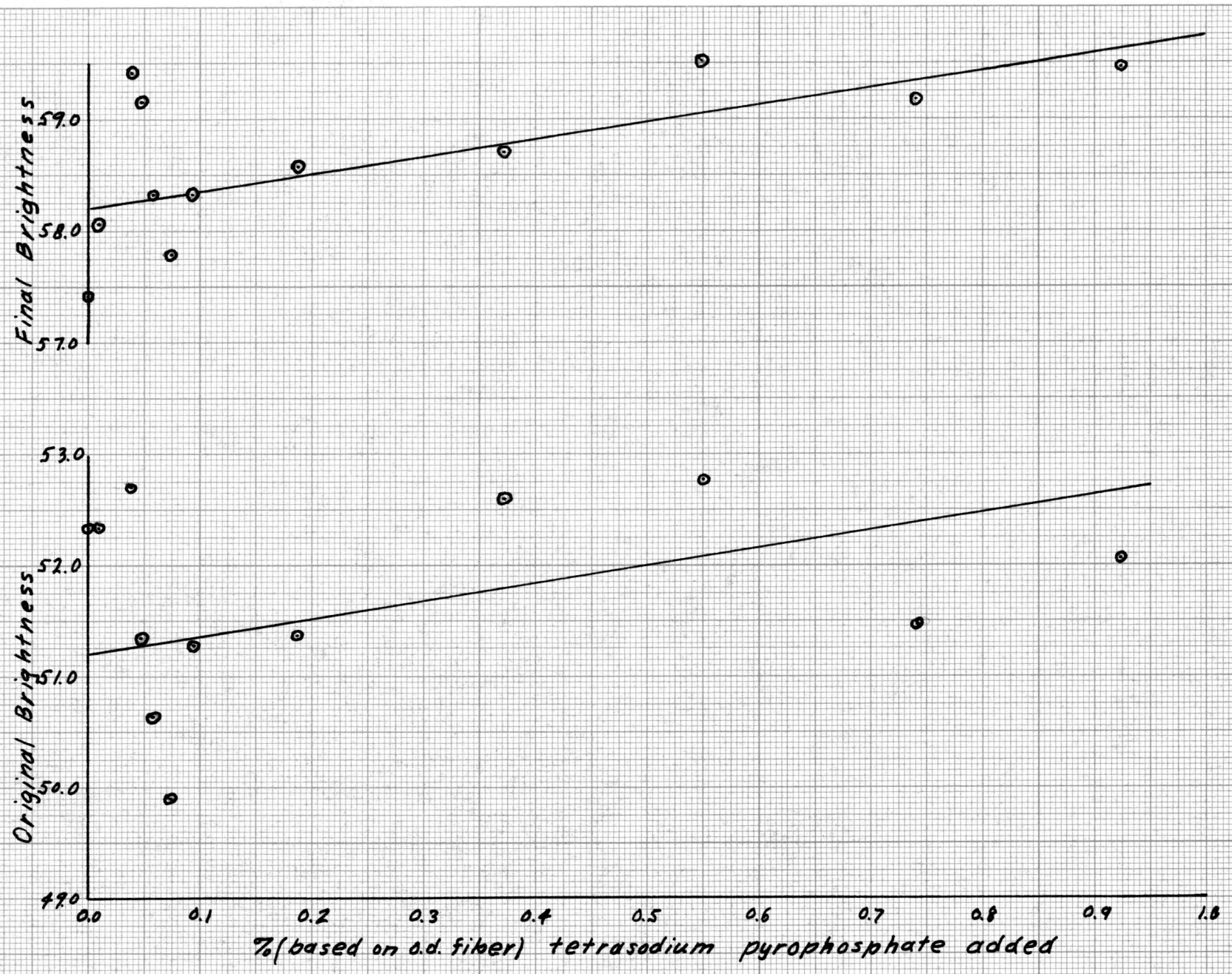
Conclusions:

1. Trisodium phosphate and tetrasodium pyrophosphate probably are effective dispersing agents in flotation deinking. Although the laboratory data gathered was erratic it definitely suggested that trisodium phosphate encourages higher brightness gains in concentrations ranging from 0.02 to 0.2 percent (based on O.D. waste paper).

2. Determinations demonstrated that froth flotation is a method of deinking by which a high percentage of mineral fiber may be saved. This can be an extremely important economic consideration in favor of flotation deinking and also aid in abating stream pollution.

GRAPH III





Recommendations, ideas and comments:

1. The literature survey of this report discusses recent literature which states that particles less than two microns are not removed by flotation deinking, particles between two and ten microns are mainly removed by flotation deinking and particles greater than twenty-five microns display extremely erratic behavior toward flotation deinking. It is very possible that further work could determine a specific flocculating agent which would flocculate those particles less than two microns and make them susceptible to flotation. The specific flocculating agent would be applied after most of the floatable material has been removed from the system.

2. Beneficial effects would possibly be derived by applying an electrical potential across flotation cells during flotation deinking.

3. To insure comparable stock in future laboratory deinking trials it would be advisable to prepare a large stock slurry in a barrel and remove constant samples for deinking after agitating the slurry.

4. Addition of alum or some other flocculating agent with some agitation just prior to handsheet formation will help precipitate the coloring matter on the fiber and should tend to give a brightness pad of more uniform brightness.

5. If carbon tetrachloride is applied to a thin air dry handsheet and the handsheet is held against a light source the formation of the handsheet may be readily observed. Chunks of stock indicate insufficient power has been applied to the stock prior to deinking.

Recommendations, ideas, and comments con't.

6. A study of flotation deinking using pH as the independent variable could possibly prove very rewarding.