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A PROPOSED METHOD OF FORMING A SODIUM
HEXAMETAPHOSPHATE FILM ON THE
FOURDRINIER WIRE

Literature Survey and Experimental Work

Senior Thesis 436 B
Western Michigan College
Curriculum in the Pulp & Paper Technology
Department

Submitted this 1st day of June, 1952

Theodore Richard Kielts

ABSTRACT

The addition of sodium hexametaphosphate to the white water system of the paper mill is an effective method of preventing pitch deposition. The ability of this compound to prevent pitch agglomeration is due to its tendency of forming monomolecular films on metallic surfaces to which pitch will not adhere.

This thesis has attempted to evaluate whether this monomolecular protective film is best formed by spraying a solution of sodium hexametaphosphate onto the moving Fourdrinier wire or whether it is best formed by the present-day method of allowing the film to form from the white water system to which sodium hexametaphosphate has been added.

The results of my experimental work have indicated that no positive conclusion can yet be made regarding this question. However, there is a tendency for better film formation by spraying. Definite conclusions, however, can be made only by further experimentation.

INTRODUCTION.

For as long as it has been in existence, the pulp and paper industry has been plagued with the problem of pitch control. In spite of the countless sums of money spent and in spite of the efforts of a very large number of trained technicians and scientists, there is still no one particular method which will eliminate pitch troubles wherever they may exist.

The purpose of this literature survey is to compile in one paper the various means resorted to in attempting to control this serious problem. It will then be possible to compare and evaluate these various methods. This author hopes that this compilation will prove to be of value for the better understanding of this problem.

THE NATURE OF PITCH.

A prerequisite for an intelligent discussion of any topic is to eliminate any possible confusion that might arise due to vague terminology or vague ideas. Therefore, it is of necessity that the term 'pitch' be defined.

One of the minute cellulosic elements found in conifers is the ray cell. It is in this cell that wood resins are produced. These wood resins consist of mainly, the water-soluble, ether-soluble, resin acid, fatty acid, ester, and unsaponifiable fractions. During the sulphite digestion process, these resins are not rendered soluble. It is during the subsequent beating operations that these ray cells are ruptured, allowing the wood resins to be brought into

colloidal suspension with the liquid phase. These particles will then agglomerate and precipitate on the paper machine forming a sticky mass. This mass is composed not only of the resins, but also of other particles occluded during their precipitation. It is this sticky mass that is called 'pitch'.

There exist two main schools of thought as to the exact nature of the agglomeration of these colloidal particles. One presumes its formation on minute dirt specks in the pulp suspension, and the other presumes a reaction involving the free fatty acids with the metallic parts of the machinery (1).

The exact constituent which causes the formation of pitch is not known, but it is known that the total ether-soluble fraction contains this unknown substance. However, progress is being made in the determination of this constituent. Richter (2) and Harris (1) both determined the composition of the ether-soluble fraction. Their results are given in the following table (1)

Table 1

<u>Constituent</u>	<u>Ether-soluble</u>		<u>Alcohol-soluble</u>	<u>Total Pulp Resins</u>	
	Richter-Harris			<u>Seasoned Pulp</u>	<u>Unseasoned Pulp</u>
Water-soluble	0.2%	8%	9%	2%	19%
Ether-soluble	--	--	0	10	11
Resin Acids	10.6	10	50	11	13
Fatty Acids	22.6	24	33	21	26
Esters	20.3	18	1	43	24
Unsaponifiable	33.3	37	7	11	6

The conclusions arrived at from the preceding table were; (a) the trouble is not due to the resin acid constituents, because of the fact that the alcohol-soluble fraction also contains resin acids (this was verified by Kress and Ragen (3) who added an excess of rosin to the beater stock), (b) the trouble may be due to the ester or unsaponifiable fraction, since a very small amount of these components were found in the alcohol-soluble fractions, and (c) from the analysis of the total resin of unseasoned and seasoned pulp, one of the chief differences between the two is a marked decrease in the ester fraction of the seasoned wood, leading to a conclusion that this may be the factor which causes pitch formation.

In addition to having a knowledge of the cause of pitch formation, it is necessary to be able to determine the amount of pitch in a pulp so that this information can be utilized by the mill in controlling pitch troubles. Kress and Nethercut (4) have developed an apparatus which can be used to give a reliable indication of the relative amount of pitchiness of a pulp. The price of the materials used in the construction of this piece of equipment enables its duplication for a reasonable sum. The principle of their apparatus is that two spirally wound wire screens, when rotated in opposite directions in a pulp suspension, will pick up the sticky mass of pitch in this suspension, and by subsequent extractions of these screens, the relative amounts of pitch can be determined. The reliability of this method is shown by the following tables.

Table 2

<u>Pitchy Pulp %</u>	<u>Non-pitchy Pulp %</u>	<u>Pickup, mg</u>
0	100	10
25	75	96
50	50	218
75	25	246
100	0	312

Table 3

<u>Pulp</u>	<u>Mill Comment</u>	<u>Ether-soluble%</u>	<u>Pickup, mg</u>
A	Excessive amounts of pitch	1.90	7.4
B	Pitchy	2.18	126.4
C	More of less trouble	2.11	110.3
D	No comment	2.56	312.3
E	No comment-3 months old	2.08	89.8
F	No comment-3 months old	0.44	14.5
G	Gives more trouble than H	2.86	3.5
H	No comment	1.07	11.6
I	No appreciable difficulties	2.30	47.6

The next logical step in this literature survey would be to present a list of methods of pitch control and to give a description of each.

PITCH CONTROL IN THE MILL

As regards methods of pitch control in the mill, they all can be assigned to two general classifications. One of these classifications concerns all of the methods of pitch control which involve the use of chemicals to reduce the deleterious factors connected with pitch formation. The other classification of methods of pitch control concerns all of the methods utilizing mechanical means in the reduction of pitch formation. The various methods will first be assigned

to their respective classifications and then they will be treated individually.

Methods of pitch control involving chemicals

1. Emulsification techniques
2. pH regulation
3. Mill water treatment
4. Addition of hexametaphosphate
5. Addition of diatomaceous silica
6. Addition of alum
7. Addition of dispersants
8. Chemical testing of pulps.

Methods of pitch control utilizing mechanical means

1. Seasoning of the wood
2. Screening operations
3. Washing operations

METHODS OF PITCH CONTROL INVOLVING CHEMICALS

EMULSIFICATION TECHNIQUES

Fritz (5) has suggested that a solvent such as kerosene be used to dissolve the pitch in the pulp suspension, and that the resulting fluid be rendered harmless by a suitable emulsifying agent. This technique is based on the assumption that one way to prevent pitch troubles is to prevent the pitch from agglomerating into sticky lumps.

In this method, two to four gallons of kerosene per ton of pulp are added to the pulp suspension prior to any mechanical treatment. When the stock is broken or refined, the liberated pitch is then immediately dissolved by the kerosene. The stabilized resulting fluid then has to be emulsified. This is best accomplished by addition of a suitable sulphonated oil emulsifying agent at the fan pump or head box, so as to allow the solvent ample time to react with the pitch that has been liberated. The ratio of one part of emulsifying agent to four parts of the pitch-solvent mass is used. After the

emulsification has taken place, the pitch is then either eliminated in the white water, or it is deposited on the fibers so as to be harmless. The emulsified kerosene leaves no residual odor in the finished product.

The limitation of this process is that the kerosene may adversely alter the sizing of the finished product. However, this same property can be utilized in the manufacture of unsized tissues. It is interesting to note that some of the emulsifiers used, although none are named, actually promote absorbency in the finished sheet.

Another method similar to the one proposed by Fritz is that of Haun (6), who suggested that acetone be used as a solvent and that the resulting fluid mass be contacted with carbon tetrachloride to separate the acetone-pitch mass from the pulp suspension.

pH REGULATION

The effect of the hydrogen ion concentration in the pulp suspension on pitch formation is not definitely known. Different investigators have come to opposite conclusions. Karlberg (7) found that by maintaining a pH between 4.4 and 5.0, by use of alum, all pitch trouble was eliminated. However, when half of the alum was replaced by sulfuric acid, pitch did appear on the doctor blades and press rolls. The fact that pH regulation by use of alum provided better protection against pitch formation than that provided by sulfuric acid can be explained by the fact that the alum, in addition to regulating the pH, also deposits the pitch on the fibers, thereby making the pitch less harmful.

On the other hand, Frazer (8) found that on a similar sulphite furnish pitch trouble was being encountered on a converted Fourdrinier machine when alum was used to maintain a pH of 4.5.

From the two conflicting reports, it would seem as if pH, as an entity, does not effect pitch formation, but rather that it does effect some factor or factors which, in turn, do promote pitch formation. However, this view is unfounded conjecture.

MILL WATER TREATMENT

Gavelin (9) has proven some interesting facts about the condition of mill water as regards pitch formation.

Table 4

<u>Source of Water</u>	<u>Hardness °dH</u>	<u>pH</u>	<u>Pitch Deposit, %</u>
1. Mill water	7.5	7.2	100
2. Mill water flocculated and filtered	7.5	"	110
3. Softened mill water	0.1	"	99
4. Artesian water	12.3	"	56
5. Distilled water	---	"	49
6. Sea water	---	"	90

From the above table the following conclusions were drawn:

1. Mill water is more harmful than distilled water.
2. The tendency to pitch formation, if viewed objectively, is not due to solid particles.
3. Removal of calcium ions by permutite treatment doesn't help.
4. Calcium, sodium, or chloride ions have no appreciable effects on pitch formation.

It was then found that by addition of calcium carbonate to the mill water pitch formation was increased, and since it was known that calcium ions have little to do with pitch formation, the cause was assigned to the carbonate ion. Efforts were then made to determine the effect of carbon dioxide on pitch formation. It was found that mill water, which has been acidified and de-aerated to remove the carbon dioxide, would allow approximately half the amount of pitch to form as would mill water which had not been decarbonated.

The above observations led to the conclusion that another method of pitch control is to decarbonate the mill water. This can be accomplished by acidification followed by aeration, or by precipitation of the carbonates by the use of a solution of calcium hydroxide and calcium chloride.

ADDITION OF HEXAMETAPHOSPHATE

Sodium Hexametaphosphate, or Calgon as it known commercially, owes its ability to combat pitch troubles to its property of being able to form a film on the metallic parts of the paper machine to which pitch will not adhere. It might be assumed that Calgon lessens pitch formation by binding the calcium ions in the mill water according to the equation;



However, it is known that the calcium ions have very little to do with pitch formation, therefore, this presumption has to be disregarded.

Gavelin (10) has shown the influence of Calgon on pitch deposits. His results are given in the following table.

Table 5

The Effect of Calgon Film on Pitch Deposits

<u>pH</u>	<u>mgs. Pitch</u>	
	<u>without treatment</u>	<u>with treatment</u>
4.5	3	1
5.0	10	4
5.5	20	5
7.0	40	6

Calgon is added directly to the white water system of the paper mill. The advantages of using Calgon, or hexameta-phosphate, are that it tends to minimize pitch formation, increases the wet strength of a sheet considerably when used under the proper conditions, and in addition, it is an inhibitor of corrosion. However, its chief disadvantage is that serious microbiological contamination of the white water system often accompanies its use.

ADDITION OF DIATOMACEOUS SILICA

The American College Dictionary defines diatomaceous earth as, "a fine siliceous earth composed chiefly of the cell walls of diatoms". The use of this diatomaceous earth in papermaking is one of the earliest methods utilized to control pitch formation. This ability of diatomaceous earth to control pitch formation is hinged on its high absorbency. It is known that the troublesome pitch is that portion of the resin which is sticky. The finely divided silica, when added to the stock in which the pitch particles are small, will coat the pitch, thus preventing further agglomeration. It is necessary that it be added before the pitch particles have a chance to form large globules, otherwise trouble will not be avoided. Pre-

sumably, the sooner the diatomaceous silica added after cooking, the greater will be its action.

The retention of this silica is very high, therefore, a minimum quantity need be used. Usually, an amount equivalent to the amount of pitch in the pulp is sufficient. An advantage of using this method of pitch control is that the pitch and the preventative both go into the sheet, thereby providing for economical and effective control (11).

ADDITION OF ALUM

This method pitch control is one which is widely employed at the present time in the paper industry. Adding alum to the stock accomplishes ^{Sp.} three things. First, it acts somewhat like a mordant in that it forms a bond between the fiber and the pitch which is deposited on that fiber. Second, it helps stabilize the emulsion, and hence minimizes pitch formation (12). Third, it decreases the bicarbonate ion content of the water, a condition which, according to Gavelin (9), tends to decrease the amount of pitch formed.

The addition of alum to the mill water for the purpose of flocculation does not tend to decrease pitch formation. Therefore, this utilization of alum cannot be considered a method of pitch control (9).

ADDITION OF DISPERSANTS

The number of dispersants used to control pitch formation is too large to treat each one individually. Diatomaceous silica, or more commonly known as Celite, was treated separately because of its prevalence. Dispersants are, generally speaking, sulfonic acid condensates. They are said to form a film around pitch particles. This film diminishes

the coalescence of the pitch, thereby preventing the troublesome agglomeration. A few of the pitch dispersants are known commercially as ; Accocel, Tamol-N, and Soda Ash.

However, it may be said that a dispersant must be tried under the conditions of the mill, as they have not experienced the same degree of success in all mills.

CHEMICAL TESTING OF PULPS

However obvious this method may seem, it must be mentioned for the sake of completeness. Since it is known that not all types of wood possess the same tendency towards pitch formation, due to the difference in their resin contents, it is logical to assume that one method of pitch control is to avoid the use of a tree specie which has this deleterious constituent. However, this is not always possible or economically practical. TAPPI provides a test for the determination of pitch in a pulp. Along with the method of Kress and Nethercut (4) as described earlier in this paper, it should be possible to predetermine the amount of pitch trouble a mill will encounter before the stock has entered the system. This might be experimentally determined by compounding an extensive series of tables which would show the relationship between pitch content of a pulp and the trouble experienced with pitch in the mill.

METHODS OF PITCH CONTROL UTILIZING MECHANICAL MEANS

SEASONING OF THE WOOD

Two possibilities exist as regards this method of pitch control. One is the natural seasoning of the wood. This can be accomplished at the mill by proper storage. It is not

definitely known how long one should season a specific type of wood to minimize pitch formation, because of the variation that exists in resin content in the various types of wood.

The other possibility is the accelerated seasoning of the wood chips. According to Harris (1), seasoning of the chips for two to three weeks is equivalent to the natural seasoning of the logs for two years. However, this seasoning of the chips is accomplished by use of considerable storage space and equipment, a fact which tends to prove this method to be uneconomical.

In both cases, the result of seasoning of the wood is that the resins are oxidized to such an extent, the tendency to pitch formation is decreased to almost an absolute minimum. This is substantiated by the decrease in ether solubility.

SCREENING OPERATIONS

Edge (13) suggests that extensive screening operations should tend to decrease pitch troubles. The reason for the postulation of this method is obvious. It is known that the greater portion of the resins is contained in the cell walls of the medullary ray fibers. These medullary ray fibers are the shortest fibered fraction of the total wood. Hence, the tendency to pitch formation should be minimized by eliminating this short fibered fraction. Edge suggests this is possible by screening the pulp suspension immediately after digestion. The weight loss would not amount to over two percent of the total weight.

WASHING OPERATIONS

Washing can be of help in controlling pitch. Sieber (14) found that of the total resin in the pulp; 4.2 % is removed by the cooking liquor, 15% in the bleach operation, and 51.8 % in the washing operation. It is evident that washing is a means of pitch control. The influence of washing can be magnified when it is done in the presence of alkali. The alkali acts as a dispersant in this case.

SUMMARY

Although there exists many methods of controlling pitch, the paper industry is still troubled with it. The reason for this is not one due to lack of initiative on the part of the paper industry. Pitch control is a delicate matter to deal with as it is characterized by many variables. Each mill has its own method of control, and due to its own peculiarities, this method probably will not solve another mills pitch troubles.

Despite this dim picture, advances are constantly being made in the understanding of the very nature and cause of the origin of pitch resins. Perhaps the solution is near at hand.

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EXPERIMENTAL WORK

THEORY

Gavelin (10) has explained that the ability of sodium hexametaphosphate to prevent pitch troubles found in the mill is due primarily to its ability of forming a monomolecular film on the metallic parts of the paper machine. This film is capable of repelling the pitch particles and thereby forces them to be carried through the machine and be included in the final sheet.

The present-day method of utilizing this monomolecular film former is to add it directly to the mill water as soon as possible after the cooking operation. This usually takes place at the beater. Now the most troublesome area of the paper machine as regards pitch deposition is the moving Fourdrinier wire. The question then naturally arises as to whether or not the beater is the best place to add the sodium hexametaphosphate. It is evident that all of the metallic parts of the paper machine system are then coated with this film. Many of those parts to which the film will deposit do not require the film at all.

Therefore, it seems as if a more efficient way of applying this film to those parts of the paper machine which need it the most can be of aid to industry.

With this in mind it was decided that it might be of value to investigate the possibilities of spraying a hexametaphosphate solution directly onto the moving Fourdrinier wire. It would then be possible to determine if this spraying is a more efficient means of forming the hexametaphosphate film where it is needed the most.

PROCEDURE

A Fourdrinier wire was obtained and it was divided into sections containing 25 square inches each. These wire sections were then used to be immersed and sprayed with hexametaphosphate solutions. Colorimetric comparisons were then made. For the colorimetric determinations the following method was used;

Stannous Chloride Method

In dilute phosphate solutions, the addition ~~to ammonium phosphomolybdate~~ of stannous chloride forms a blue complex.

Required-- Nessler tubes, ammonium molybdate, and stannous chloride solutions.

To a 50 ml. sample, free from color and turbidity, add, with mixing, 2 ml. ammonium molybdate solution and 0.25 ml. of stannous chloride solution. After 5 minutes, compare colorimetrically with standard solutions made at the same time.

In each trial, the wire screen was exposed to a hexametaphosphate solution of a concentration of six parts per million. This includes the screens which were immersed and those which were sprayed. The procedure used for the immersion tests was as follows;

The above concentration of hexametaphosphate solution was made up to one liter. The wire screen was then immersed for periods ranging from 5 minutes to 2 hours. The solution was then agitated by means of a magnetic stirrer. The phosphate was then stripped off of the wire by using 50 ml. of 10;1 nitric acid. The wire screen was rinsed off with 50 ml. of distilled water. The colormetric determination was then made.

The procedure followed for the spraying tests were as follows;

The wire screen was suspended beneath a rubber hose, which had been pricked to form uniform holes. Air pressure was then introduced into a flask containing the hexametaphosphate solution and this solution was then forced through the rubber hose and out the slits. This produced a very fine spray. Spraying was carried on for 5 minutes to 2 hours. The screen was then stripped of the phosphate film in the same manner as those screens used in the immersion tests. Colormetric determinations were made.

It was decided that the colormetric determinations be of a qualitative rather than of a quantitative nature. The immersion and spraying tests were run at the same time and were compared at the same time.

SUMMARY AND CONCLUSIONS

During the above process of comparisons it became evident that;

1. The hexametaphosphate film was poorly formed by either spraying or immersion when the solution was not in contact with screen for more than 45 minutes.
2. After a 45 minute period the immersion method proved to yield a higher amount of phosphate as evidenced by the deeper blue color in the colormetric tests.
3. As the length of treatment proceeded, however, the spraying method tended to equal and pass the amount of film deposition as provided by the immersion method.

It is impossible to come to any definite conclusion, however, because of the fact that I did not obtain 100 % reproduceability of the above results. Therefore, only further experimentation can determine if spaying a hexametaphosphate solution onto the Fourdrinier wire yields a better film than one which is obtained by the present method of adding the sodium hexametaphosphate directly to the beater.