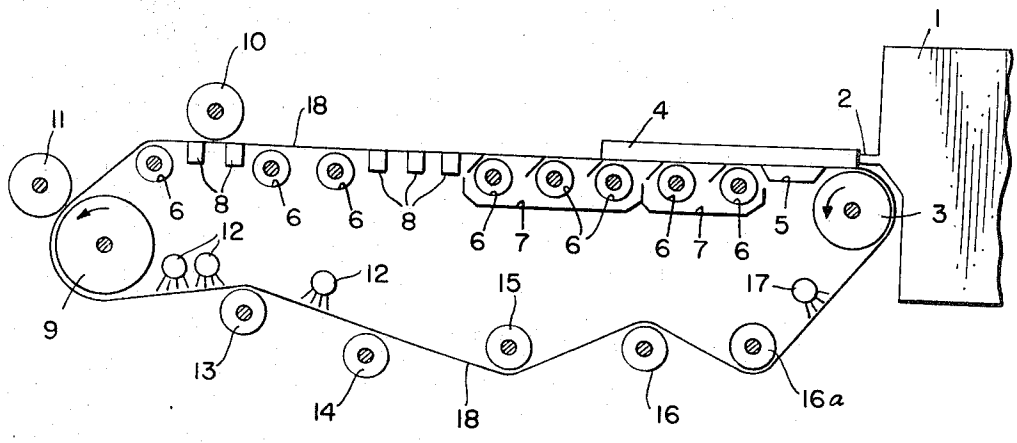
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R. J. MICHALSKI

3,316,176

PAPER MAKING PROCESS

Filed Feb. 12, 1964



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PAPER MAKING PROCESS

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1 Claim. (Cl. 252—47)

This invention relates to a method for improving by chemical means the operational efficiency of a Fourdrinier paper making machine. More specifically, the invention is concerned with extending the life of Fourdrinier wires commonly employed in Fourdrinier paper making machines.

One of the most versatile machines used in the manufacture of paper is the well-known Fourdrinier paper making machine. Utilizing machines of this type, a wide variety of paper products are produced in mills located throughout the entire United States. Such conventional paper and paper products as bags, building boards, paper boards, various book stocks, and such specialized paper products as carbon paper stocks, cigarette papers, glassine and greaseproof papers, napkins, newsprint, pulp, tissue, wrapping, and writing stocks may be produced on Fourdrinier machines.

As Fourdrinier machine technology has been improved over the years, there has been an increased tendency to use Fourdrinier machines which operate at extremely high speeds. While high speed Fourdrinier paper making machinery enables the mills using such machines to produce large tonnages of various types of paper and paper products, there is a disadvantage encountered in that the abrasive wear of the Fourdrinier wire used in the machine is excessive. The life of a typical Fourdrinier wire, particularly in a high speed machine, is short. In some instances, Fourdrinier wires only last several days whereas in other cases, particularly on slower speed machines, it is possible for a Fourdrinier wire to last for as long as several weeks to a month or more. In complex Fourdrinier machines, Fourdrinier wire replacement becomes an expensive and time consuming operation when it is considered that production must stop and elaborate procedure must be followed in order to replace the Fourdrinier wire. Depending upon the particular type of paper being produced on the machine, the cost of a new Fourdrinier wire can range up to more than $5,000, or more. When the wire costs are considered in conjunction with labor costs required to install Fourdrinier wires, it is readily apparent that any method, either chemical or physical, for reducing wire loss by extending the life of a Fourdrinier wire without sacrificing speed or production would be a valuable benefit to the paper making industry.

Numerous mechanical solutions to Fourdrinier wire wear have been proposed. They have met with only limited success. Most mechanical systems for improving Fourdrinier wire life involve the installation of expensive rolls and tension regulating devices, and to this end their installation is only practical in the design of new machinery and is not particularly adaptable to existing Fourdrinier machines. A practical approach to the problem of reducing the wear and extending the life of Fourdrinier wire resides in the use of chemicals whereby the wire may be treated at low economical dosages, either intermittently or on a continuous basis, to substantially increase its operating life.

For a chemical treatment to effectively improve the life of Fourdrinier wires, it is necessary that it perform several vital functions which will tend to alleviate the basic problems which cause Fourdrinier wire wear. Metallographic examination of worn Fourdrinier wires has

made it evident that there are numerous factors which effect wire life. One of the most common factors causing Fourdrinier wire failure is the abrasive wear caused by a friction between the bottom of the wire and the suction boxes, forming boards, and deflectors. Most of this wear occurs at the suction boxes. A serious form of abrasive wear comprises the burring of the bottom of the wires, particularly the warp knuckles.

Other types of wear in Fourdrinier wire may be ascribed to frictional effects and present themselves as worn wire in the forms of scores and distortions. Frequently, excessive wire wear may be attributed to poor drainage characteristics, either because of improper vacuum on the suction boxes or other similar reasons. Also, a poor quality water will cause scaling and edge filling. Similarly, due to mechanical characteristics of the wire, edge cracks, edge splits, and edge distortion frequently occur in Fourdrinier wires operating on various types of Fourdrinier machines.

A factor which sometimes tends to accelerate abrasive wear of Fourdrinier wires is corrosion. The corrosion effects tend to substantially reduce abrasion resistance and draining characteristics of the wire so that frictional effects imposed on the wire are increased.

A careful study of the above types of wear of a Fourdrinier wire leads one skilled in the art to the obvious conclusion that if abrasive wear or frictional properties of Fourdrinier wire, caused by its contacting the various parts and sections used in a Fourdrinier machine, could be reduced and if the drainage characteristics of the wire could be improved, thereby preventing blockage by either fiber or foreign substances, then a practical solution to the extension of Fourdrinier wire life could be achieved. Therefore, if a chemical treatment is to succeed in improving the operation characteristics of a Fourdrinier paper making machine by the extension of the useful life of the Fourdrinier wire used in such machines, such a treatment should function in a twofold manner. First, and most important, it must be capable of preventing abrasive wear by providing a lubricating action on the wire. Secondly, it should act as a dispersant or cleansing agent to prevent or to remove deposits between the open areas defined by the mesh of the particular wire used. Copending commonly assigned applications having Ser. Nos. 161,701, now U.S. Patent No. 3,150,035 and 161,702, now U.S. Patent No. 3,140,222 filed Dec. 22, 1961, disclose two suitable methods for substantially increasing Fourdrinier wire life. However, there is a continual demand in the paper industry to extend the operational life of high speed Fourdrinier to even longer periods of time. Considerable savings are effected with realization of each additional day of wire life without necessity of replacement. If a chemical treatment in modification of either of the above two processes could achieve the aim of even longer continual periods of wire operation and particularly by further decreasing wire abrasion, it would find ready acceptance in the paper art.

It therefore becomes an object of the invention to provide a combination chemical treatment, which when applied in low, economical dosages, will improve the operational efficiency of a Fourdrinier paper making machine to an extent heretofore unachieved.

Another object of the invention is to provide a chemical composition which will substantially reduce the abrasive wear of Fourdrinier wires and measurably extend wire life to longer periods than is possible by existing treatment. Other objects will appear hereinafter.

In accordance with the invention it has been found that the operational life of a Fourdrinier papermaking machine may be greatly improved by treating the bottom of a wire with a combination of chemicals comprising (A) a water soluble, sulfhydryl-containing, extreme pressure lubricant and (B) an unsaturated 5-membered nitrogen heterocycle

containing 2–4 nitrogen atoms constituting ring members of the heterocycle. By using this combination of ingredients, it is possible to substantially increase the life of Fourdrinier wire by addition thereto of as little as 0.005 pound of the combination treating agent per ton, based on the weight of the paper found on the wire.

It had previously been determined that the above extreme pressure lubricant aids to prolong Fourdrinier wire life. It has a twofold effect in that lubricity is afforded and drainage of the stock formed is improved, thereby providing a surface which has less tendency to abrade than an untreated wire passing over the various sections of a typical Fourdrinier machine. It is believed that localized areas of stress are excessive to the point that high pressures are involved in the use of the Fourdrinier wire. Conventional lubricants, therefore, are of little value in the solution of the problems enumerated above. Also employment of conventional lubricants often leads to the serious problem of excessive slippage on Fourdrinier machine rolls, and may otherwise deleteriously affect the the paper process. It had been found necessary to employ an extreme pressure lubricant. It had also been found that of such materials, the ones mentioned above as components of the invention in this case, unexpectedly increased wire life when applied at and above levels of .005 pound per ton of paper on the wire.

It has now been determined that a relatively minute amount of a 5-membered nitrogen heterocycle when added to the above specified extreme pressure lubricant, gives a surprising increase in wire life in comparison to the sole use of that same extreme pressure lubricant. In some instances, as much as a 50% increased efficiency occurs, in terms of increased percentage of prolonged wire life, by addition of the combination of two chemicals to the wire. Such results are obtained even though the chemical combination is applied in the same total dosage as is the extreme pressure lubricant when employed as a sole reagent.

For a more comprehensive understanding of how the compositions of the invention are applied to improve the operational characteristics of a Fourdrinier machine, reference may be had to the drawing.

The drawing is a simple schematic diagram of a typical Fourdrinier end of a paper making machine. The numerals used in the drawing represent the various components of the Fourdrinier system. It is to be understood that the drawing is simplified, but serves to illustrate generally a typical Fourdrinier system. The headbox and slice area are generally represented by the numerals **1** and **2** respectively. The breast roll is illustrated by the numeral **3** whereas the deckle rolls and forming board are shown by the numerals **4** and **5**. The table roll **6**, tray **7**, and suction flat boxes **8** are another common group of components found in Fourdrinier machines.

The couch roll **9**, dandy roll **10**, and lump breaker roll **11**, might be considered as ending the top section of a typical Fourdrinier assemblage. Wire showers **12**, wash rolls **13**, automatic guide rolls **14**, stretch rolls **15**, and wire return rolls **16** and **16A** all compose what is generically referred to herein as the return section of the Fourdrinier wire, and operate to control the bottom movement of the wire. The wire itself is indicated by the numeral **18**. An important concept of the invention resides in the use of a shower applicator **17** which is located between a wire return roll **16A** and the breast roll **3**. This shower spray is a preferred application point for applying the wire life extending chemicals of the invention. It is obvious that the spray **17** should be positioned so that it uniformly sprays the chemicals onto the entire width of the wire **18**.

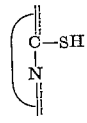
To be effective, it is desirable that the chemical be applied to the bottom of the wire. The word "bottom" is used to refer to any point in the return section of the Fourdrinier wire between the couch roll **9** and its point of subsequent contact with the breast roll **3**. This wire "bottom" section is admirably suited for application of the treating agent. It is preferable that the application point be as near the breast roll as possible.

An alternative method of applying the chemicals of the invention would be to coat the chemicals by suitable means (not shown) on the wire return roll **16**, whereby the bottom of the wire would be coated uniformly. Regardless of the mode of application, it is important that the entire wire **18** be covered with the chemical and that the chemical be applied in the form of a dilute aqueous solution.

From the above description it is apparent that the chemicals in the invention are most preferably applied as a dilute aqueous solution to the bottom of the wire just prior to its engagement with the stock entering from the headbox **1** through the slice **2**. The application of a dilute aqueous solution may be achieved by dissolving the chemicals into a suitable water source (not shown) and thereby applying them through the header or spray **17**. The chemicals may be prepared initially either as dry chemicals to be subsequently diluted at the mill site or point of use, or they may be made up into an aqueous concentrate for efficiency in shipment to the mill site where it may be diluted by the machine operators.

The water-soluble, extreme pressure lubricants are sulfhydryl-containing compounds. They may be classified broadly as nitrogen-containing heterocyclic compounds characterized by a ring nitrogen bonded to a ring carbon. To the ring carbon is attached a non-ring sulfhydryl group. The characteristic structural formula covering this sulfhydryl heterocyclic combination of elements may be illustrated by the Formula I below:

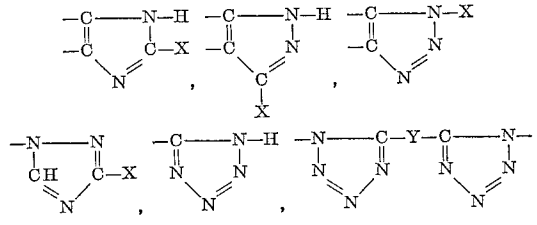
FORMULA I



Compounds having this illustrative molecular configuration and which are valuable in the practice of the invention are such well-known compounds at 2-mercaptothiazole, 2 - mercaptobenzimidazole, 2 - mercaptobenzoxazole, and 2-mercaptobenzothiazole. Of these compounds, 2-mercaptobenzothiazole is preferred since it is relatively inexpensive and is commercially available.

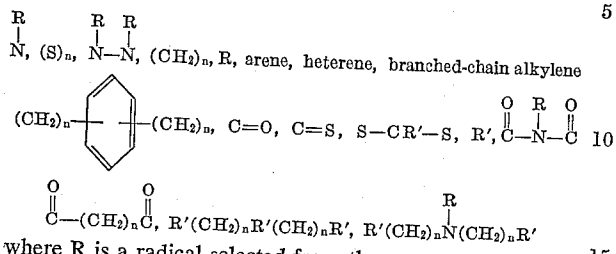
The above compounds are, for practical purposes, relatively water-insoluble, but they are rendered readily soluble by converting them to their alkali metal salts. Any of the well-known alkali metal salts of these compounds, e.g., sodium, potassium, cesium, and rubidium may be used, although due to availability and economics, the sodium salts are preferred. Equivalent to the sodium salts of these compounds are the ammonium salts, but they are not particularly preferred due to volatility problems encountered when the machines are operated at elevated temperatures.

Greatly preferred 5-membered nitrogen heterocycles are water-soluble and have a nucleus selected from among the following nuclei:



and tautomers thereof wherein X is a radical selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, alkylol, alkenyl, alkythio, amino, aminoalkyl, aminoaryl, aminoalkenyl, hydroxyl, heteryl, haloalkyl, haloalkenyl, haloaryl and nitroaryl, free valence bonds in said nucleus being satisfied by members selected from the group consisting of alkyl, aryl, hydrogen, aralkyl, alkylol, alkenyl, phenylene, substituted phenylene, heteryl, heteralkyl, alkoxy, and halogenated derivatives thereof, amino, substituted amino, alkamino, alkenyl amino,

amido, halogen, alkester, nitramino, azo, carbamyl, guanylamino, acylamino, substituted amido, hydrazo, alkylthio, arylthio, nitroaryl, and aralkylthio, and Y is a spacing grouping radical selected from the group consisting of:



where R is a radical selected from the group consisting of alkyl, hydrogen, alkaryl, aryl, alkylol and alkenyl, R′ is either sulfur or oxygen and *n* is an integer of from 0 to 6.

The following are typical five-membered ring nitrogen heterocycles falling within the above general structural formula which may be used in combination with the extreme pressure lubricants.

The following are typical five-membered ring nitrogen heterocycles which may be used in combination with the extreme pressure lubricants.

TABLE I

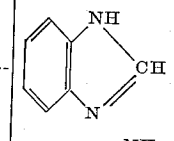
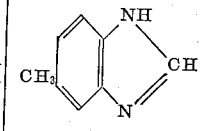
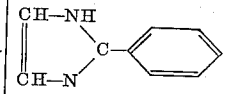
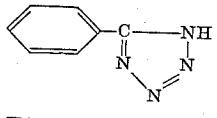
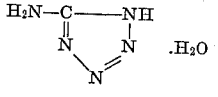
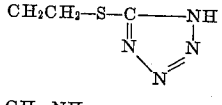
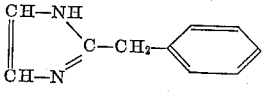
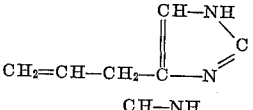
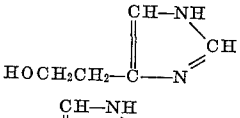
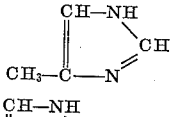
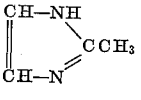
No.	Formula	Name
1		Benzimidazole.
2		5-methyl benzimidazole.
3		2-phenyl imidazole.
4		5-phenyl-1H, tetrazole.
5		5-amino-1H, tetrazole.
6		5-ethylthio tetrazole.
7		2-benzyl imidazole.
8		4-allyl imidazole.
9		4-(β-hydroxyethyl) imidazole.
10		4-methyl imidazole.
11		2-methyl imidazole.

TABLE I—Continued

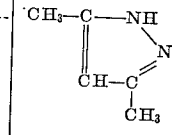
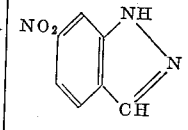
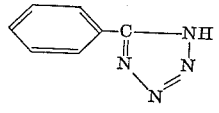
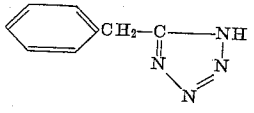
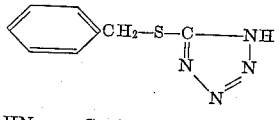
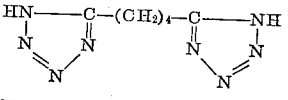
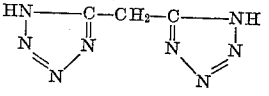
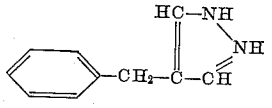
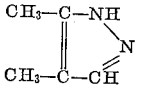
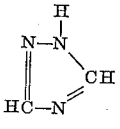
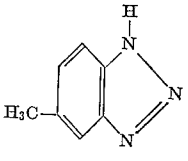
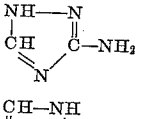
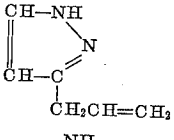
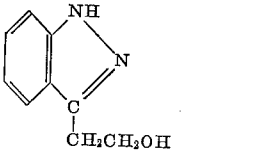
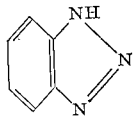
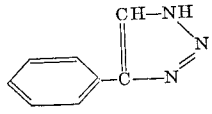
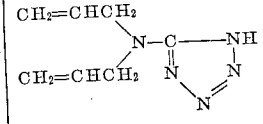
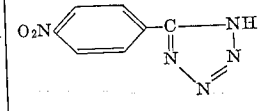
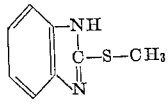
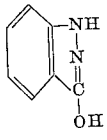
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12		3,5-dimethyl pyrazole.
13		6-nitroindazole.
14		5-η nitrophenyl-1H, tetrazole.
15		5-benzyl-1H, tetrazole.
16		5-benzylthio-1H, tetrazole.
17		5,5′-tetramethylene, bis tetrazole.
18		5,5′-methylene, bis tetrazole.
19		4-benzyl pyrazole.
20		4,5-dimethyl pyrazole.
21		1,2,4 triazole.
22		5-methylbenzotriazole.
23		3-amino-1H-1,2,4-triazole.
24		3-allyl pyrazole.
25		3-(β-hydroxyethyl) indazole.

TABLE I—Continued

No.	Formula	Name
26		Benzotriazole.
27		4-phenyl-1,2,3-triazole.
28		5-diallylamino-1H, tetrazole.
29		5-*p*-nitrophenyl-1H, tetrazole.
30		2-(methylthio) benzimidazole.
31		3-indazolinone.

The more preferred compounds among those just listed are benzotriazole and substituted derivatives thereof, tetrazole and substituted tetrazoles such as amino-tetrazoles and specifically 5-amino-1H, tetrazole, and bis-tetrazoles such as 5,5'-tetramethylene bis-tetrazole or 5,5'-methylene bis-tetrazole. Of these the most preferred is benzotriazole.

One or more of any of the above listed 5-membered nitrogen heterocycles or others falling within the scope of the invention may be used in combination with the sulfhydryl-containing extreme pressure lubricant chemicals to greatly improve Fourdrinier wire life.

It has been discovered that best results in prolonging wire life are achieved when specific ratios of extreme pressure lubricant to the above previously defined nitrogen heterocycle compounds are employed. In laboratory evaluations it was found that the effectiveness of a wire life extension treatment may be measured in a simple test known as a potentiometric determination. It appears that those compositions which give optimum results in terms of prolonging wire life are materials which exhibit the greatest power of film tenacity or adherence to the wire. Compositions which are maintained in a tightly adherent state or in close contact with the wire thereby hold their lubricating power and ability to keep the wires from plugging over long periods of time. They thus keep the wire in a clean and unabraded condition. In short, the greater the tenacity of the film imparted to the wire by the chemical treatment, the longer a wire is able to remain in use without replacement.

The degree of film tenacity is readily measured by determing the potential difference or driving force between anodic and cathodic sites on the surface of a copper electrode, which is required in order to obtain a specific current density. The driving force requirement is determined by measuring the potential difference between the anodic and cathodic polarization curves at the same current density. The higher the driving force at any one current density, the higher the filming tenacity of the chemicals under test. In turn, the degree of filming is directly related to optimum realization of prolonged wire life. The magnitude of the potential difference, then, is directly proportional to the efficiency of a chemical combination in prolonging Fourdrinier wire life.

Table II below shows the increase in driving force or potential difference at various currents due to the effect of the chemicals present. The measurements were taken in a simulated paper mill white water having a pH of about 4.5. In each case, though the ratio of the two chemicals was varied, the total amount of the combination of the two added to the water was maintained at about 10 ppm.

The particular combination involved in this experiment was 2-mercaptobenzothiazole (MBT) and 1,2,3-(1H) benzotriazole (BZT). Ratios were adjusted throughout a broad range in order to determine the optimum MBT/BZT ratio. From the experimentation it is evident that the most preferred range of ratio of the two chemicals of MBT to BZT is from about 7.5:1 to about 10:1. The highest driving forces at each measured current were obtained between this range of proportions of the two chemicals. The same effect was noted with respect to others of the above specified extreme pressure lubricants in combination with various 5-membered heterocyclic nitrogen ring compounds. The driving force in terms of millivolts realized at various chemical ratios and at certain currents are listed below in Table II.

TABLE II.—MBT/BZT RATIO

Current	10.0/0	20.0/1	10.0/1	9.0/1	8.5/1	7.89/1	7.0/1	0/10.0	0/0
1	175	140	160	245	280	185	145	160	15
2	230	225	240	325	420	285	210	230	20
5	310	365	380	450	595	500	320	365	25
10	405	505	520	605	725	640	430	415	30

In a greatly preferred embodiment a dispersing agent is added in conjunction with the extreme pressure lubricant and 5-membered nitrogen heterocycle. The dispersant acts to further reduce wire plugging by maintaining proper drainage. Typical dispersing agents may include aliphatic polyalkylene polyamines wherein at least one nitrogen is substituted with an aliphatic group of from 12–22 carbon atoms in chain length, carboxylic and inorganic salts of the foregoing, such as acetates, sulfates, chlorides, and the like, aliphatic monoamines such as N-dodecyl amine, N-tetradecyl amine, dicoco amine, N-hexadecyl amine, N-octadecyl amine, etc. Other amine dispersants may be alkylene diamines such as the "Duomeens" including such commercially available chemicals as N-lauryl trimethylene diamine, N-coco trimethylene diamine, N-soya trimethylene diamine, and N-tallow trimethylene diamine. Imidazolines are also useful as water-dispersible cationic dispersants. These compounds are well-known and are described in Wilson U.S. Patents 2,267,965 and 2,355,837. Typical imidazolines include 1-(2-aminoethyl)-2-heptadecyl imidazoline and 1-(2-hydroxyethyl)-2-heptadecyl imidazoline. Clausen U.S. Patent 2,865,817 comprehensively describes imidazolines of the type which may be used as dispersants.

In addition to the above discussed cationic dispersants or others, anionic or non-ionic detergents or dispersants may be likewise used with equal success. Among these the well-known alkaryl sulfonic acids and their alkali metal salts, such as sodium dodecyl-benzene sulfonate

may be used as well as the alkali metal salts of sulfonated alcohols and the sulfonated lignins. A preferred class of non-ionic materials are the alkyl substituted ethoxylated phenols such as ethoxylated dodecyl phenol. Other suitable non-ionic dispersants or wetting agents are the well-known "Pluronic" materials which are block copolymers of propylene and ethylene oxide and are described in U.S. Patent 2,674,619.

A typical composition of the invention contains 80–99% by weight of extreme pressure lubricant and nitrogen heterocycle and 1–20% by weight of dispersant, both percentages being based on total weight of the two classes of materials.

The compositions of the invention may either be formulated as a dry mix and then diluted at the point of use, or preferably, they are prepared as an aqueous concentrate which is then diluted to use concentration. Typical aqueous concentrates contain 5–60% by weight of extreme pressure lubricant plus nitrogen heterocycle and 0.1–10% by weight of dispersant.

In testing the Fourdrinier wire to provide increased life during its normal operation the chemicals are fed at a relatively low dosage, e.g., .005 pound per ton based on the dry weight of the paper formed on the Fourdrinier wire with the preferred dosage being from 0.025 to 0.1 pound per ton. The chemical additives may be slug-fed or continuously applied to the wire.

A typical composition useful in the practices of the invention is the aqueous concentrate illustrated by Formula II below:

FORMULA II

Ingredient:	Percent by weight
73% sodium hydroxide	11.3
2-mercaptobenzothiazole	19.5
1,2,3-(1H)benzotriazole	2.0
Anionic dispersant	1.0
Water	66.2

To illustrate the invention, the following are presented by way of example. It is to be particularly noted in the following examples that an unexpected increase in wire life is realized by inclusion of the 5-membered nitrogen heterocycle with the extreme pressure lubricant. This is to be compared to like runs of same total dosage involving sole use of an extreme pressure lubricant.

Example I

This test was conducted on a Fourdrinier machine which produced 600 tons per day of unbleached kraft multiwall bag paper. The machine, prior to the test without benefit of any wire life extender chemical had an average wire life of about 6–7 days. Inspection of the wires after removal from the machine showed that abrasion was the primary source of wire wear. 2-mercaptobenzothiazole was applied at a dosage of 10 p.p.m. The chemical was applied by means of a shower spray at a point just prior to the breast roll. After a period of 13 days the wire had to be replaced. In a second test at the same location and run under the same conditions, 10 p.p.m. of the Formula II chemical was applied. During this test a series of wires ran for 21–24 days before shutdown was necessitated.

Example II

At another paper mill Formula II was tested on a Fourdrinier machine producing groundwood sulfite specialities. The output of the machine averaged between 200 and 400 tons per day. During the test period the Fourdrinier wire was run at speeds ranging from 1100 to 2100 feet per minute. The pH of the white water system was between 5.0 and 7.0. The previous average wire life was 7–9 days.

A series of wires were treated with 10 p.p.m. of 2-mercaptobenzothiazole. The chemical was applied from a shower header located across the wire bottom at a point between the return roll and a breast roll. At the end of the test the average wire life was 12–14 days.

The above was then compared with Formula II. Again 10 p.p.m. of this composition was employed and applied as described above. During this test run the average wire life was approximately 17 days.

In addition to increasing Fourdrinier wire life, the compositions of the invention also keep the wires extremely clean and bright. Stock drainage characteristics of the papermaking operation were materially increased. The most important benefit achieved was decrease in abrasion. It is believed that this factor is the most important single cause for wire life failure after short periods of time. As auxiliary effects of the invention a better quality of paper is produced, and faster drying and sheet formation is realized through application of the compositions of the invention. Greater variations in refining and machine speeds are also permitted.

The invention is hereby claimed as follows:

A composition useful in improving the operational efficiency of a Fourdrinier papermaking machine which comprises 7.5–10.0 parts by weight of 2-mercaptobenzothiazole and one part of benzotriazole.

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