NRL REPORT C-3394

FILTER PAPER STUDIES V
EFFECT OF VISCOSE FIBER PROCESSING

Harold W. Knudson

Hollingsworth and Vose Company
East Walpole, Massachusetts

December 7, 1948

Approved by:

Dr. E. A. Ramskill, Head, Protective Chemistry Section
Dr. P. Borgstrom, Superintendent, Chemistry Division

NAVAL RESEARCH LABORATORY
CAPTAIN H. A. SCHADE, USN, DIRECTOR
WASHINGTON, D.C.

DISTRIBUTION

	Copy No.
BuShips	
Attn: Code 688	(1-7)
BuMed	(8-9)
ONR	
Attn: Code N482	(10-11)
Dir., USNEL	(12-13)
Med. OinC, NMRI, Bethesda	(14-15)
CO, Radiation Laboratory, Naval Shipyard, San Francisco, Calif.	(16-17)
Atomic Energy Commission	
Attn: Technical Library	(18-20)
OCSigO	
Attn: SIGTM-S	(21)
CO, SCEL	
Attn: Dir. of Engineering	(22-23)
Chemical Corps, USA	
Attn: Office of the Chief	(24)
Attn: Technical Command, Army Chemical Center	(25-26)
Attn: Med. Div., Army Chemical Center	(27)
Attn: CO, Naval Unit, Army Chemical Center	(28)
Attn: CO, Camp Detrick, Frederick, Md.	(29-30)
Hollingsworth and Cose Company (Via CO, ONR, Boston)	(31-32)
RDB	
Attn: Technical Library	(33-34)
Attn: Navy Secretary	(35)
Science and Technology Project	
Attn: Mr. J. H. Heald	(36-37)
NRL Secret File Room	(38-52)

PREFACE

This Naval Research Laboratory report consists of the following two Research and Development Reports written by H.W. Knudson of the Hollingsworth and Vose Company, East Walpole, Massachusetts, on Navy Contract N7-ONR-430.

> "Research and Mill Trial on the Development of a Domestic Substitute for Esparto Fiber in the Navy Type H-60 Filter Paper," Third Quarterly Period of Contract N7-ONR-430, referred to as the N-9 Trial.

> "Research and Mill Trial on the Development of a Domestic Substitute for Esparto Fiber in the Navy Type H-60 Filter Paper," Fourth Quarterly Period of Contract N7-ONR-430, referred to as the N-10 Trial.

This report concludes the work on the first year of the contract. Filter paper studies are being continued by the Hollingsworth and Vose Company under a renewal of the contract. Additional reports will be published when received.

This page intentionally left blank.

CONTENTS

ABSTRACT

Two mill runs (N-9 and N-10 trials) and the associated laboratory research work are described under the general program for making an improved type of Navy H-60 filter paper.

The N-9 trial is concerned essentially with the optimum physical and chemical conditions for causticizing the viscose furnish, a great part of this laboratory study being concerned with the type and degree of washing that may produce a satisfactory product. It is demonstrated that a hydropulper, a piece of equipment commonly found in paper mills to defiber paper stock, will materially aid in the causticization procedure. Operating conditions such as temperature, caustic concentration, and degree of agitation are extremely important when causticizing stock in this equipment.

The N-10 trial is concerned essentially with a study of the effect of blending causticized rope fibers with causticized rayon. Upon substituting 50 percent of the rayon with the causticized rope, there resulted a paper with markedly improved handling properties and with only a small decrease in efficiency.

PROBLEM STATUS

This is an interim report on this problem; work is continuing.

AUTHORIZATION

NRL Problem C04-28R.

RESEARCH AND MILL TRIAL ON THE DEVELOPMENT OF A DOMESTIC SUBSTITUTE FOR ESPARTO FIBER IN THE NAVY TYPE H-60 FILTER PAPER (N-9)

INTRODUCTION

This report is a summary of the work done for the third quarterly period of Contract N7-ONR-430 (January 1, 1948 to March 31, 1948). A statement of the general objectives and an outline of previous work accomplished are contained in past reports of this series.*

The mill trial reported here is designated as the N-9 trial, H & V Lot No. 315, dated February 10, 1948.

Reference to the N-7 and N-8 trials (NRL Report C-3299) will show that causticized viscose not only serves as an excellent substitute for esparto in type H-60 filter paper but promises to lead to a new and very superior filter material. From the N-8 mill trial, it was learned that viscose could be causticized in

---

* H.W. Knudson, "Filter Paper Studies I. Effect of Replacing Esparto with Yucca Fiber," NRL Report C-3172, September 1947.

H.W. Knudson and S. J. Pasternak, "Filter Paper Studies II. Effect of Replacing Esparto with Wood Pulp Fiber," NRL Report C-3225, January 1948.

H.W. Knudson and S. J. Pasternak, "Filter Paper Studies III. Effect of pH and Added Electrolytes," NRL Report C-3226, January 1948.

H.W. Knudson and S. J. Pasternak, "Filter Paper Studies IV. Effect of Replacing Esparto with Viscose Rayon Fiber," NRL Report C-3299, June 10, 1948.

the beater with considerably less difficulty than in the rotary boiler. However, both these pieces of equipment leave something to be desired in the handling and treating of viscose stock.

From the past two mill trials it was found that there existed at times a considerable difference between viscose causticized in the laboratory and that causticized in the mill. It was felt that a more detailed study should be undertaken to explain these differences.

It was also recognized from the earlier mill trials that all of the caustic must be removed from the treated fibers before satisfactory paper could be made. Since this required a rather long and involved procedure, a second object of this study was the investigation of the effect of acid neutralization in an attempt to shorten the washing time.

Commercially available cut rayon flock contains a great many fiber bundles which remain unopened after going through the flock cutting machinery. The fibers in these bundles are held together very loosely, but these bundles have been the source of trouble in the causticizing process. When furnished to the beater in a caustic solution, these fibers tend to fuse together still more and give rise to "fiber pills" in the finished paper, resulting in a somewhat reduced filtering efficiency. A third object of this study, therefore, was to eliminate these "fiber pills" from the finished paper.

LABORATORY WORK

Repeated laboratory causticizing with 8 percent sodium hydroxide at a rayon consistency of 4 percent resulted in excellent fiber which when felted with asbestos produced a filter material having a high efficiency. It was felt that the laboratory procedure produced uniformly satisfactory results and that the difficulties experienced in mill practice were due to deviations from this practice. A careful review of the laboratory procedure showed that equally good results could be obtained by causticizing either in the laboratory beater or in the Waring Blendor, provided that other factors were controlled. A preferred method is the treatment of the rayon flock with 8 percent caustic at 4 percent consistency in a Waring Blendor for 15-30 seconds, after which the stock is poured into three times its volume of water for quenching. The resulting fiber is collected on a wire screen and thoroughly washed by repeatedly diluting and dewatering on a wire screen. It was further observed that if the agitation in the Blendor was continued for a much longer period of time (3-5 minutes), the fibers tended to gelatinize too much and the washing became much more difficult if not almost impossible. The same general observations were made with stock treated in the laboratory beater, although the time intervals were longer due to the less drastic or different type of agitation.

Nonfibrous Rayon

The above facts led to a microscopic study of the fiber slurries at the different phases of this study. In all cases where the stock had been diluted with water, it was observed that the fibers were surrounded with varying amounts of "regenerated" nonfibrous flakes and agglomerates of viscose. In general there was a greater quantity of this nonfibrous material and the agglomerates were larger when the causticizing period was long and the agitation was vigorous. It was reasoned that the caustic partially dissolves or, at least, softens the outside portion of the fiber, and with continued high agitation, particularly under a beater roll, this soft portion is rubbed off or dissolved. Upon dilution this portion of the viscose reappears in nonfibrous form. Whereas washing to approximate neutrality had previously been taken as the index to complete washing, it was demonstrated in these studies that stocks containing a large proportion of nonfibrous material could be washed to neutrality long before all the nonfibrous material was removed.

It then became necessary to show that the presence of this nonfibrous material was objectionable or that it accounted in some degree for the difference between filter paper made in the laboratory and that made in the mill. This could not be demonstrated completely until the time of the mill trial, but the effect of leaving varying amounts of this nonfibrous cellulosic material in handsheets was observed. With increasing amounts of this material left in the stock, standard handsheets showed increasing tensile strength and air resistance, and decreasing efficiencies. Very poorly washed stock resulted in handsheets that were very harsh and almost brittle. It is postulated that this nonfibrous component cements the fibers together to show increased tensiles and at the same time plugs up some of the interstices to show a high air resistance and low efficiency.

It is evident from this preliminary work that the stock prepared in the mill would have to be washed as free as possible from this undesirable material to match the performance of laboratory-treated stock. It was also demonstrated that washing the treated stock free of caustic to a neutral pH was not an adequate index of complete washing. Some other control such as a microscopic examination or the air resistance of a standard viscose handsheet would be better.

Acid Washing

Considerable attention was given to the problem of washing the caustic out of the treated stock, because this step was very time consuming in the mill beaters. It will be remembered from the N-8 mill trial that the treated and diluted stock was machined over the Fourdrinier wire and removed as wet-lap. This process removed a large proportion of the caustic, but the wet-lap still had to be washed for a considerable time after being returned to the beater. It was felt that this wet-lap could be furnished to a weakly acidified beater of water in order to reduce the washing time necessary for caustic elimination.

For the purpose of determining the effect of acid neutralization, if any, on the finished filter paper, three laboratory trials were made. The following viscose furnish was used in each case:

75%----1.5 denier - 1/8" long

25%----1.5 denier - 1/4" long

Trial No. 1

The laboratory beater was filled with an 8 percent caustic solution and furnished with the viscose flock to about 4 percent consistency. With the beater roll raised, the stock was circulated for approximately 15 minutes. The fiber was then quenched by pouring the beater charge into three times its volume of water. The stock was then thoroughly washed on a wire screen with large volumes of water.

Trial No. 2

The viscose was causticized and quenched in water as in Trial No. 1 and was then collected on a wire screen and formed into wet-lap. This lap was added to a weak acid solution (HCl) such that a neutral solution resulted. The stock was then washed free of salt.

Trial No 3

The stock was treated the same as in Trial No. 2 except that an excess of acid was used and then the fiber was washed free of the acid and salt.

Effect of Acid-Washed Viscose on Filter Characteristics

To analyze effects of the different washing procedures on the paper characteristics, the following filters were made from Blue Bolivian asbestos and the washed viscose for a series of tests.

Sample 1 --- 25% B.B. Asbestos + 75% Viscose of Trial No. 1
Sample 2 --- 25% B.B. Asbestos + 75% Viscose of Trial No. 2
Sample 3 --- 25% B.B. Asbestos + 75% Viscose of Trial No. 3

Physical Tests

Typical physical data are recorded below.

Sample	Tensile (Unpressed) lb./inch @ 130 lb. R.W.
1	1.8
2	1.7
3	1.8

From the above data it appears that there exists no appreciable difference in the tensile strengths of the filters made from the viscose treated as indicated. It should be noted that the recorded tensiles are for handsheets that were not wet pressed hence are lower than the tensiles that might be expected from a machine made paper.

Filtration Tests

Table I is a summary of typical smoke filtration performance of the filters.

TABLE I

Performance Data of Papers Made from Acid-Washed Viscose

Sample	DOP Penetration* (%)	Resistance* (mm H_2O)	Efficiency† (%)
1	.001	127	3.94
2	.003	115	3.73
3	.004	112	3.73

*Measured by NRL Smoke Penetration Meter E2, E2R1, or E3. For operating instructions see NRL Instruction Manual A 825A, "Instructions for Canister Tests, Part II Filters, Section A, Smoke Penetration," 13 July 1945.

†Percent efficiency $= \frac{-\log P}{R} \times 100$, where P is the DOP penetration expressed in decimals rather than percent, and R is the resistance across the sample in mm of water under the standard conditions of test.

Apparently there is no noticeable difference in the smoke filtration efficiency between the above samples.

"Break" Tests

Following is a summary of "break" data on these samples. It appears that all samples exhibited good resistance to "break."

TABLE II

Effect of DOP Exposure on Performance

Sample	Property Measured	Time in Minutes			
		0	1	3	5
1	Resistance (mm H_2O)	113	114	114	115
	DOP Penetration (%)	.005	.006	.006	.006
2	Resistance (mm H_2O)	117	117	118	118
	DOP Penetration (%)	.004	.003	.004	.004
3	Resistance (mm H_2O)	113	114	115	115
	DOP Penetration (%)	.005	.006	.005	.006

Performance vs Flow Rate

Table III is a summary of performance rates of 85, 42½, and 21¼ liters per minute. It is evident that in all cases, good asbestos distribution and mechanical perfection were obtained.

TABLE III

Performance vs Flow Rate

Sample	Flow Rate					
	85 1/m		42½ 1/m		21¼ 1/m	
	Res ($mm\ H_2O$)	DOP Pen (%)	Res ($mm\ H_2O$)	DOP Pen (%)	Res ($mm\ H_2O$)	DOP Pen (%)
1	118	.003	59	.001	30	.000
2	118	.003	59	.001	30	.000
3	112	.004	56	.002	28	.001

Discussion of Acid Washing

From the preceding data it would appear that neutralization of the caustic in the stock during final washing could be accomplished by the addition of dilute acid (HCl) without any appreciable effect on performance. However, it is known that if any residual acid remains in the sheet, the viscose fiber will be tenderized when heated or aged.

It should also be noted that laboratory work done by A.D. Little, Inc. subsequent to the N-9 mill trial revealed other variables which might be introduced by the acid treatment. Only a preliminary statement can be made at this time. Based on microscopic observations, they report some evidence that when the wet-lap is put into a dilute acid solution the nonfibrous portion tends to agglomerate to larger particles which are less easily washed out of the stock than the finer dispersion of the same material. They also report some evidence that the extent of the crinkle in the fiber is lessened by the acid treatment. If the acid treatment continues to show processing advantages, the deleterious effects of agglomerates and crinkle should be investigated further.

Fiber Pills

As mentioned earlier in this discussion, some concern has been expressed over the formation of "fiber pills" in the viscose stock. The obvious solution to the elimination of these "fiber pills" would be to eliminate the fiber bundles in the rayon flock before the caustic treatment. On a laboratory scale this was accomplished by repeatedly passing the fiber through a vacuum cleaner and collecting the flock in the filter bag. Handsheets made in the laboratory from this flock showed the presence of no "fiber pills."

However, no blower equipment of this design was available for mill work, so it was impossible to completely eliminate the "fiber pills" in the N-9 trial. In consultation with the flock cutters, it was learned that they might possibly "blow" the flock, but it was represented to be an operation which would materially add to the cost.

Subsequent to the N-9 trial, more time was spent in the laboratory on this problem. The agitation of a Waring Blendor seemed better suited for this purpose than a beater, so attention was centered on this apparatus. These studies lead to the belief that the "fiber pills" could be eliminated by the careful adjustment of caustic concentration and temperature when agitated by a Waring Blendor or similar equipment. The optimum caustic concentration for this type of agitation seemed to be closer to 7.0 percent NaOH than the 8.0 percent commonly used in the beater. Moreover, the influence of temperature seemed to be much more critical than had been observed previously in the beater. The optimum temperature seemed to be between 60° and 70°F, probably 65°F. In addition to controlling the extent of the "fiber pills," it seemed possible to more accurately control the causticizing treatment.

Hydrapulper

The advantages of agitation produced by the Waring Blendor suggested the use of the hydrapulper, a piece of equipment commonly found in paper mills for defibering paper stock. Being similar to a Waring Blendor, the hydrapulper can substitute for the beater in the causticizing treatment on a commercial scale. The only hydrapulper available at this company is much too large for the limited amount of rayon fiber available for this study, so arrangements were made at the Dilts Machine Works, Fulton, New York to use their semi-commercial unit (four feet in diameter). Three separate trials were conducted in this small hydrapulper by a representative of Hollingsworth and Vose Company working with a representative of A.D. Little, Inc.

From preliminary studies in the Waring Blendor, the following three conditions were chosen for the hydrapulper trials.

TABLE IV

Causticizing Treatments in Hydrapulper

Trial	Rayon Flock (lb)	Consistency (%)	Concentration of Caustic Solution (%)	Temperature (°F)	Time (min)
No. 1	36	4	7.0	55	2
No. 2	36	4	7.0	65	2
No. 3	36	4	7.0	70	2

It will be observed that the temperature was varied from $55^{\circ}F$ to $70^{\circ}F$ while all other conditions were held constant. At the end of the two-minute agitation in each case, the entire charge was dumped into three times its volume of water for quenching. Samples of the fibers were collected and washed before being returned to this laboratory for examination. Samples from Trial No. 1 were difficult to wash free from regenerated viscose agglomerates; those from No. 2 and No. 3 washed much easier. Handsheets made from each of these three trials showed a progressive difference. Those made from No. 1 revealed a generous amount of "fiber pills;" the fiber was well crinkled, the sheets were somewhat harsh, and the air resistance was quite high. Those made from No. 2 revealed no "fiber pills," the fiber was well crinkled, the sheets were soft, and the air resistance was low. Those made from No. 3 revealed no "fiber pills," the fiber was poorly crinkled, the sheets were very soft and had little mechanical strength, and the air resistance was likewise low.

These studies were very informative and suggested the use of a hydrapulper instead of a beater for this process. With violent agitation in the hydrapulper, careful control over temperature, caustic concentration, and time seem to be imperative. At the present, 4 percent fiber consistency, 7.0 percent caustic solution, $65^{\circ}F$, and 2 minutes agitation seem to be optimum conditions for operation in a hydrapulper.

If further trials in the beater fail to offer the same advantages as those of the hydrapulper, serious consideration should be given to the use of a hydrapulper of proper size and design.

THE MILL RUN

Furnish

On the basis of the above experimental data, it was decided to make a machine run with a furnish of:

25% Blue Bolivian asbestos

75% Causticized viscose flock

75 parts of 1.5 denier - 1/8" long
25 parts of 1.5 denier - 1/4" long

The viscose would be causticized in a beater at an 8 percent caustic concentration and a viscose consistency of 4 percent. This slurry would be diluted 3:1 in water and run over the Fourdrinier wire to be removed as wet-lap. The lap would be returned to the beater for an acid (HCl) wash.

Preparation of Stock for Mill Trial

A predetermined amount of 8 percent caustic solution (NaOH) was made up in the beater and 375 pounds of 1.5 denier - 1/8 inch flock and 125 pounds of 1.5 denier - 1/4 inch flock were added to the beater just in front of the rotating roll, which was in the raised position throughout the entire operation. The resulting consistency was approximately 4 percent. The stock was circulated and samples were taken periodically. After 30 minutes the fiber was causticized to the proper degree. The caustic mass was dropped with agitation into three times its volume of water in the beater chest.

To remove the caustic, the slurry was sent over the Fourdrinier wire and was removed as wet-lap. At this point the lap was returned to the beater with a total of 90 pounds of muriatic acid (31 percent HCl).

Following is a summary of the washing data:

TABLE V

Summary of Washing Procedure

Time	pH	Resistance @ .035" thickness (mm H_2O)	Remarks
7:30	10.0	23	Start of washing after first acid addition
8:00	10.5	23	
8:30	10.5	11	
9:00	2.8	8	Second acid addition
9:30	4.2	8	
10:00	5.5	7½	
10:30	6.0	4	
11:00	6.0	4	Dropped beater

From the above data it appears that after causticizing and at a high pH, the fibers do not felt into a porous pad as indicated by the initial resistance of 23 mm. That this resistance was not entirely a function of pH is shown by the fact that after the pH was changed from 10.5 to 2.8, the resistance decreased only slightly probably in direct proportion to the washing. When the wash water was examined it was found to contain small, nonfibrous globules of regenerated viscose. Evidently during causticizing some viscose is dissolved or torn from the fibers and reappears with dilution. Washing was continued until the major portion of these globules of viscose were removed as indicated by the final resistance and examination under the microscope. Prior to dropping the beater, the wash was examined and only a negligible amount of these globules was found.

The yield of causticized fiber was approximately 300 pounds (about 60 percent). In actual production this yield may be increased somewhat with an increase in amount treated, since there is a certain minimum loss for a given quantity of fiber treated in this manner, and naturally this percentage loss would be smaller the larger the starting batch.

Manufacturing Data

After washing, the causticized viscose was dropped to the beater chest. The beater was furnished with 54 pounds of Blue Bolivian asbestos which was given a hard beat for approximately 30 minutes after which it was well defibered. The asbestos was dropped into the beater chest and thoroughly mixed with the viscose.

The resulting furnish consisted of:

300 lb	Causticized viscose	85%
54 lb	Blue Bolivian asbestos	15%
354 lb		100%

The stock was "backed-up" in the Jordan (sent through under pressure with the Jordan plug backed off) to obtain thorough mixing and was sent to the machine to be felted into paper. Approximately 10 percent more asbestos was added to the stock from the auxiliary asbestos feed line as the stock was fed to the Fourdrinier.

The calender stack was set up so that one light roll could be used to soften up the sheet. No great difficulty was experienced in the formation and handling of this paper over the machine once the machine was set up to allow for the high shrinkage of the sheet during drying.

Performance of the Paper

Average values of physical tests of this paper are recorded below. Allowance should be made for possible inaccuracy in these low ranges of tensile strength.

Caliper ----	0.032 in.
Ream weight-	124 lb
Tensile (length)	3 lb
Moisture --------	3.6%

A record of the smoke filtration performance of the paper is tabulated in Table VI.

This data indicates the performance of a very good filter paper. Though the efficiencies recorded in Table VI are not exceptionally high, they are well within the range set by the past causticized viscose furnishes.

Effect of DOP Exposure

Table VII shows the effect of DOP exposure on smoke penetration. The rate of "break" was exceptionally slow and entirely satisfactory.

TABLE VI

Performance Data of Mill Run Samples

Sample	Resistance ($mm\ H_2O$)	DOP Penetration (%)	Efficiency (%)	Comment
1	90	.075	3.47	1 Nip
2	95	.045	3.53	
3	92	.055	3.54	
4	100	.022	3.66	Added Asbestos
5	101	.024	3.58	
6	92	.054	3.56	
7	98	.020	3.78	1 Nip
8	97	.022	3.77	
9	96	.040	3.59	

TABLE VII

Effect of DOP Exposure on Performance of N-9 Trial Sample

Time of Exposure (Min)	Resistance ($mm\ H_2O$)	DOP Penetration (%)
0	99	.049
1	99	.044
3	100	.044
5	100	.045

Performance vs Flow Rate

Following is a summary of performance vs flow rate for this paper.

TABLE VIII

Performance vs Flow Rate of N-9 Trial Sample

Flow Rate (l/m)	Resistance ($mm\ H_2O$)	DOP Penetration (%)
85	103	.042
42½	52	.028
21¼	26	.011

The above data show a normal decrease in penetration with flow rate which indicates that good formation, good asbestos distribution, and no pin holes were realized in this paper.

Relaxation with Aging

The possibility of relaxation with aging--increased penetration accompanied by small decreases in resistance--was checked and typical results are recorded in Table IX. No relaxation was observed after aging for 30 days.

TABLE IX

Effect of Aging on Performance of N-9 Trial Sample

Interval After Manufacture	Resistance (mm H_2O)	DOP Penetration (%)
None (sample A)	93	.045
None (sample B)	96	.050
30 days (sample A)	93	.044
30 days (sample B)	96	.045

DISCUSSION

It will be recognized that it is not always possible in a mill trial to duplicate the optimum conditions as indicated by work in the laboratory, however, it is believed that a closer approach was made to these conditions in the N-9 trial than in any other trial using the viscose furnish.

Several important variables such as concentration of caustic temperature and agitation in the causticizing treatment and acid washing were studied during this period. At this time it is not possible to state whether or not present mill equipment on hand is adequate to control these variables. In the meantime an effort is being made to investigate the advantages of other standard equipment which might be better suited for the purpose.

It should be pointed out at this time that arrangements have been made by A.D. Little, Inc. to install a rental unit of an Oliver vacuum filter at Hollingsworth & Vose for the purpose of learning if equipment of this type is better suited for washing the stock than present methods.

***

RESEARCH AND MILL TRIAL ON THE DEVELOPMENT OF A DOMESTIC SUBSTITUTE FOR ESPARTO FIBER IN THE NAVY TYPE H-60 FILTER PAPER (N-10)

INTRODUCTION

This report is a summary of the work done for the fourth quarterly period of Contract N-7-ONR-430 (April 1, 1948 to June 30, 1948). A statement of the general objectives and an outline of previous work accomplished are contained in past reports of this series.*

The mill trial reported here is designated as the N-10 trial, H & V Lot No. 518, dated July 8, 1948.

Reference to the N-7 and N-8 and to the N-9 trial (first part of this report) will show that gas mask filter papers made in part from a causticized viscose rayon furnish have higher filtering efficiencies than papers made from any other fiber furnishes yet tried. However, a number of difficulties in handling this kind of stock in a paper mill make it impossible to recommend without reservation its adoption at this time for replacement of the esparto type furnish for H-60 Navy Filter Material. It should be made clear, however, that these difficulties are of a practical nature and it is assumed that they can be overcome with more experience and proper processing equipment.

Thus far in attempts to causticize rayon flock, treatment of the fiber has been carried out in a rotary boiler and also in a standard type paper mill beater. Both of these pieces of equipment lack important features which would permit the accurate control of time, temperature, and concentration of the causticizing action. The importance of controlling these variables is recognized now more than ever.

It was stated in the N-9 trial that consideration should be given to the use of a hydrapulper for causticizing the rayon flock. The advantages of a hydrapulper for this purpose still seem to be unmistakable, so arrangements have been made through a contract with the Office of Naval Research to purchase and install in the West Groton mill of Hollingsworth and Vose Company one Type HC 8-foot Hydrapulper made by the Dilts Machine

---

* NRL Reports C-3172, C-3225, C-3226, C-3229.

Works, Fulton, New York. Because of slow delivery on certain electrical equipment, it is expected that operation of this machine will be delayed for six months or more.

In the meantime research work and mill trials will continue under the current contract in an effort to establish and control the variables more accurately and to improve the processing techniques for the manufacture of this material. Consideration will also be given to the possibility of blending other fibers with the causticized rayon flock when advantages can be recognized.

LABORATORY WORK

Some of the difficulties encountered in the manufacture of the causticized rayon sheet undoubtedly result from inadequate control of temperature, concentration, and time in the causticizing treatment. Over-causticizing results in low yields, difficult washing problems, and in a finished filter material having a stiff harsh feel with poor bending or folding characteristics as well as low filtration efficiencies. The mechanical strength is usually high, but the abnormal shrinkage on the driers invariably leads to numerous breakdowns of the paper on the drying cans and almost impossible running conditions. Under-causticizing, on the other hand, leads to a stock which shows higher yields and one which is more easily washed. However, the mechanical strength of the finished paper is very low and this again results in numerous breakdowns of the paper on the drying section of the paper machine and on the rewinder. Although the scuff resistance is poor, the filtration efficiency is usually high.

In each of the two cases of inadequate causticizing control cited above, one of the major problems is that of breakdowns on the paper machine. Although it can be anticipated that better control can be available with installation of a hydrapulper, the abnormal shrinkage on the paper machine will probably always be a source of annoyance in the manufacture of this paper where the base furnish consists of 100 percent causticized rayon flock.

It seemed advisable therefore, to investigate in the laboratory the possibility of finding a long fiber compatible with the rest of the furnish which could be used effectively to "dilute" the rayon in the furnish and thereby lessen the shrinkage. It was realized at the outset that some sacrifice in filtering efficiency might have to be made but the other advantages might be important enough to allow a slight decrease in efficiency.

A review of much of the work done in connection with the development of H-60 filter paper and subsequent research suggested the possible use of causticized kraft wood pulp (NRL Reports C-3225 and C-3226). Laboratory handsheets made with a portion of the causticized rayon replaced by causticized kraft showed a marked decrease in shrinkage on drying, but the resultant mechanical strength was so low that it seemed unwise to study this fiber further.

It was believed that a long fiber such as rope fibers commonly used in paper manufacturing would be more suitable if they could be rendered softer and processed without hydration. Rope fibers are used in the present H-60 furnish and have also been used in the rayon furnish of the N-7 trial (NRL Report C-3299). However, it has never been possible to employ more than 5-10 percent rope in the furnish without very seriously impairing the filtering efficiency. In view of the relative success in improving the performance of other fibers by a causticizing treatment, it was decided to investigate the use of causticized rope fibers.

It might be argued that rope fibers like manila, sisal, and other hemp fibers do not represent a domestic source of raw materials for the manufacture of this filter paper. This is true in part, but it should be pointed out that the source of this raw material for paper making is usually in the form of old rope. Old rope in the past has existed in large inventories in this country for paper making and it can be assumed that equally large stock piles will exist in the event of another emergency.

At first it was thought that it might be possible to causticize the manila fibers in the beater at the same time and along with the rayon. However, after making a few handsheets from stock treated in this way, it was decided that the rope would have to be treated with a higher concentration of caustic than was normally employed for the rayon. Various concentrations of caustic were tried for the treatment of the manila. Optimum results seemed to be realized at about 12 percent caustic with a solution-to-fiber ratio just sufficient to wet out the fibers thoroughly. This varied from 5:1 to 8:1 depending upon the type of vessel and agitation that was available. Little effect was observed by varying time, temperature, and caustic ratio over the range normally encountered in mill practice. When caustic solutions of less than 12 percent were used, the fiber was not judged to be as suitable. Concentrations greater than 12 percent did not seem to improve the performance.

Although there was not enough time to investigate completely all variables in the causticizing treatment of manila fibers, the preliminary investigation indicated that reproducible results could be obtained. It was therefore decided to make up a series of handsheets in which varying proportions of causticized rayon would be replaced by causticized manila.

Old manila rope which had previously been cooked in the rotary boiler for normal preparation into papermaking fibers was used throughout this investigation. The fibers were in pulp form having been washed and defibered in the beater. This pulp was treated with a 12 percent caustic solution at 65°F in the ratio of about 7 parts solution to 1 part dry fiber. After 10 minutes, the fibers were washed on a screen until free from caustic. The viscose was causticized with a 7.5 percent solution at 65°F in a Waring Blendor for 5 seconds after which it was quenched and washed. A stock solution of defibered Blue Bolivian asbestos was prepared in the normal way.

From these prepared fibers, handsheets were made in which the rope-viscose ratio was varied over a wide range. Table I shows the performance characteristics of these handsheets.

TABLE I

Effect of Furnish Composition on Performance of Handsheets

Furnish: Rope (wt %)	Furnish: Viscose (wt %)	Asbestos (wt %)	Resistance (mm H_2O)	DOP Penetration (%)	Efficiency (%)
0	100	28	214	.010	3.23
25	75	28	108	.025	3.35
25	75	28	109	.026	3.29
50	50	25	101	.044	3.33
50	50	28	109	.023	3.34
50	50	28	113	.026	3.18
50	50	28	113	.023	3.22
50	50	28	101	.035	3.43
75	25	28	108	.028	3.29
75	25	28	118	.024	3.08
75	25	28	120	.018	3.12
100	0	28	124	.030	2.85

The efficiency of the sheet decreases as the rope content of the furnish reaches 100 percent. On drying these handsheets it was observed that shrinkage decreased markedly for furnishes containing 25 percent and more causticized rope.

Break Tests

From Table II, showing the effect of DOP exposure on smoke penetration, it appears that the samples exhibited very good resistance to "break".

TABLE II

Effect of DOP Exposure on Performance of Sample Handsheets

Furnish: Rope (wt %)	Furnish: Viscose (wt %)	Asbestos (wt %)	Zero Exposure: Res (mm H_2O)	Zero Exposure: DOP Pen (%)	2-min Exposure: Res (mm H_2O)	2-min Exposure: DOP Pen (%)	5-min Exposure: Res (mm H_2O)	5-min Exposure: DOP Pen (%)
0	100	28	125	.009	126	.009	125	.010
25	75	28	122	.022	123	.018	125	.016
75	25	28	122	.020	122	.022	123	.022
100	0	28	124	.032	125	.032	126	.030

Performance vs Flow Rate

Table III is a summary of performance at various flow rates. It is evident that there was good asbestos distribution in the sheets, and that there was no evidence of "pin-holes."

TABLE III

Performance vs Flow Rate of Sample Handsheets

Furnish		Asbestos (wt %)	Flow Rate (l/m)	Resistance (mm H_2O)	DOP Penetration (%)
Rope (wt %)	Viscose (wt %)				
0	100	28	85	124	.009
			42½	62	.008
			21¼	31	.004
25	75	28	85	112	.022
			42½	56	.020
			21¼	28	.010
50	50	28	85	110	.027
			42½	55	.026
			21¼	27.5	.014
75	25	28	85	116	.026
			42½	58	.028
			21¼	29	.016
100	0	28	85	124	.028
			42½	62	.030
			21¼	31	.018

Physical Tests

Table IV records typical physical data of sample handsheets. It appears that there is no appreciable difference in the tensile strengths of the filters made with various percentages of rope content. These handsheets were not wet pressed, hence the tensiles are lower than those which might be expected on machine-made paper.

DISCUSSION OF CAUSTICIZATION CONTROL

One of the most important considerations involved in this mill trial was the effect of concentration and temperature when causticizing viscose.

When making up the caustic in the mill, a 50 percent sodium hydroxide solution is used. This caustic soda is added to less than the actual amount of water in the beater needed for the desired concentration. Then water is added to dilute the solution to the exact percentage wanted. During the addition of the caustic, the temperature rises anywhere between 15° and 20°F.

TABLE IV

Physical Properties of Sample Handsheets

Furnish			Physical Data	
Rope (wt %)	Viscose (wt %)	Asbestos (wt %)	Caliper (in.)	Tensile (#/inch width)
0	100	28	.044	1.80
25	75	28	.043	2.00
25	75	28	.045	2.25
50	50	25	.045	1.60
50	50	28	.043	1.70
50	50	28	.042	1.75
50	50	28	.042	1.50
50	50	28	.043	1.40
75	25	28	.043	1.60
75	25	28	.043	1.70
75	25	28	.045	1.50
100	0	28	.046	1.60

In former mill trials this temperature rise was not appreciated to the fullest extent, partly due to the low temperature of the river water during cold months. The operating conditions of former trials did not exceed a temperature of 65°F. It was known that the water temperature during this mill trial would be about 60°-65°F at the start. With caustic added to this, the final make-up solution in the beater would have a temperature between 75-80°F. This would result in an operating temperature higher than any previous mill run.

This problem was studied in the laboratory. Several caustic solutions of various concentrations were made up. At each of the concentrations, viscose was causticized at several temperatures. At the same time, a convenient stock hydrometer was calibrated for each concentration and temperature. Rayon flock was then causticized under each of the chosen conditions and handsheets were made up from the treated fibers.

An attempt was made to choose the best handsheets representing the optimum caustic concentration at each temperature. Temperatures ranged from 65°F to 85°F. At temperatures of 80°F and higher, small charges (¼-½%) in caustic concentration had little effect on performance of the handsheets. It should also be mentioned that at temperatures higher than 80°F, this preliminary study indicated that strength characteristics were sacrificed. However, more laboratory work will be required to establish this observation.

Data representing the above studies were tabulated and graphed for quick reference during the mill trial. For any temperature between 65°F and

80°F there appeared to be an optimum caustic concentration, although the physical strengths of handsheets appeared to decrease somewhat as the temperature increased. At temperatures above 80°F, the data should be repeated.

THE MILL RUN

Furnish

On the basis of the above information, it was decided to make a mill run using the following furnish:

50% Causticized rope (Manila)

50% Causticized rayon flock

75 parts of 1.5 denier-1/8" long

25 parts of 1.5 denier-1/4" long

To this would be added approximately 25 percent Blue Bolivian asbestos on the weight of the base furnish. The choice of 50 percent causticized rope was arbitrary.

Preparation of Stock for Mill Trial

The beater was furnished with 125 pounds of Blue Bolivian asbestos and beaten hard for approximately 30 minutes until it was well defibered. This asbestos was then dropped into the beater chest where it would later be mixed with the rest of the furnish. Another 25 pounds of asbestos was likewise prepared and pumped to the auxiliary chest for bleeding in at the head box as required.

It was anticipated that the operating temperature for causticizing the rayon flock would be approximately 80°F. On the basis of previous laboratory studies, it was decided to use an 8.25 percent solution of caustic in the beater, however, due to an oversight, the final concentration actually used was approximately 8.0 percent. To the caustic in the beater was added 525 pounds of rayon flock (75 parts 1.5 denier - 1/8 in. long; 25 parts 1.5 denier - 1/4 in. long), the beater roll being in the raised position during the entire operation. The consistency was about 4 percent. The stock was circulated and samples were taken periodically. At the end of 20 minutes the causticizing action was judged to be complete, although the fibers were slightly under-causticized.

The beater was then dumped into a chest containing three times the beater volume of water. After this quenching the stock was pumped over the Fourdrinier machine and removed as wet-lap which was then returned to the beater for final washing. After 1-1/4 hours of washing with warm water, the pH was lowered to 7.8. The yield was 360 pounds or 68.5 percent. (It is interesting to note that this yield is higher than normal and is probably due to the lesser degree of causticization at the higher temperature.) This stock was then dropped to the beater chest containing the previously prepared asbestos and allowed to circulate while about 300 pounds of causticized rope was furnished to the beater.

The rope stock used in this mill run was processed previous to the time of the trial. The rope was first subjected to a "normal" caustic cook in a rotary boiler using a 7 percent NaOH solution in the ratio of 8 parts by weight of solution to 1 part by weight of the dry fiber. The contents of the boiler was cooked at 40 pounds steam pressure for a period of 8 hours. The cooked stock was then washed in a beater and pumped to the drainers. It was then returned to the boiler and causticized at room temperature with a 12 percent caustic solution for 1 hour. Then the weight ratio between caustic solution and dry fiber was 7 to 1. The treated rope was washed again in the beater and pumped to the drainers. On the day of the mill trial this rope stock was defibered in the beater and dropped into the beater chest to be thoroughly mixed with the viscose and asbestos. The quantity of causticized rope fiber used was about 300 pounds.

Manufacturing Data

With all the constituents of the paper furnish in the beater chest, the resulting furnish consists of:

360 lb	Causticized viscose	55%
300 lb	Causticized rope	45%
660		100%

Added to this was 125 pounds Blue Bolivian asbestos.

The stock was sent through a Jordan under pressure with the plug backed off to obtain thorough mixing and was sent to the machine to be made into paper. Approximately 4 percent extra asbestos was added to the stock from the auxiliary asbestos feed line as the stock was fed to the machine.

The calender stack was set up so that one light roll could be used to soften up the sheet. No difficulty was experienced in the formation and handling of this paper over the machine once the machine was set up.

Performance of the Paper

Average values of physical properties of this paper are recorded below. The tensile is somewhat low but allowance should be made for possible error in these low ranges of tensile strength.

Caliper ----------0.038 in.
Ream Weight ------- 138 lb
Tensile (length)----1.0 lb
Moisture -- --------3.8%

A summary of the smoke filtration performance of the paper is shown in Table V.

The Jordan plug was set up intentionally during the middle of the trial in an attempt to increase the tensile strength. However, it can be seen from Table V that the efficiency was materially reduced. Of the paper

TABLE V

Performance Data of Samples Taken Directly from Paper Machine

Sample	Resistance (mm H_2O)	DOP Penetration (%)	Efficiency (%)	Remarks
1	103	.046	3.23	Adding asbestos No Jordan
2	115	.020	3.21	
3	110	.024	3.29	
4	140	.010	3.14	Set up Jordan
5	138	.013	2.82	
6	145	.009	2.79	
7	112	.070	2.81	Slight Jordan Less asbestos
8	108	.075	2.89	
9	104	.084	2.96	
10	125	.012	3.13	Jordan off More asbestos
11	138	.004	3.19	
12	117	.014	3.29	
13	120	.013	3.24	Less asbestos
14	116	.016	3.27	
15	110	.026	3.25	

made with the Jordan plug out, the efficiencies check closely with those obtained on laboratory handsheets made with the same furnish.

Effect of DOP Exposure

Table VI shows the effect of DOP exposure on smoke penetration. The rate of "break" was higher than that observed on similar handsheets but is regarded to be satisfactory for a paper containing as much as 50 percent causticized rope.

TABLE VI

Effect of DOP Exposure on Performance of N-10 Trial Sample

Time (min)	Resistance (mm H_2O)	DOP Penetration (%)
0	115	.020
5	121	.035

Performance vs Flow Rate

Following is a summary of performance vs flow rate for this paper.

TABLE VII

Performance vs Flow Rate of N-10 Trial Samples

Flow Rate (l/m)	Resistance (mm H_2O)	DOP Penetration (%)
85	110	.024
42½	55	.017
21¼	28	.009

The above data show a normal decrease in penetration with flow rate which indicates that good formation, that is, good asbestos distribution and no "pin-holes" were realized in this paper.

Effect of Aging

Whenever possible, samples of mill trial filter material are retested several weeks after manufacture to see if any relaxation occurs on storage. In the past, some samples have been observed which show a lower air resistance and higher smoke penetration on standing. Table VIII shows the performance of the N-10 paper at the time of manufacture and two weeks later. There is no evidence that this paper relaxes on standing for two weeks.

TABLE VIII

Effect of Aging on Performance of N-10 Trial Sample

Sample	Date of Manufacture		Two weeks later	
	DOP Penetration (%)	Resistance (mm H_2O)	DOP Penetration (%)	Resistance (mm H_2O)
1	.071	108	.075	105
2	.056	101	.055	101

DISCUSSION

Pending the installation of a hydrapulper, work was continued on the beater process for causticizing rayon flock. The temperature of the process water has risen sharply since the last mill trial in the spring. An effort was made to compensate for the higher temperature by increasing the caustic concentration, but preliminary studies indicate that some sacrifice in physical strength of the finished material is to be expected.

A more important object of the present work was to study the effect of blending causticized rope fibers with the causticized rayon. The object was twofold. In the first place, it was hoped that the abnormal shrinkage of the causticized rayon on drying would be reduced to a point where it would be less troublesome on the paper machine. In the second place, it was hoped that the long rope fibers would add to the mechanical strength of the finished paper.

Using 50 percent causticized rope fibers and 50 percent causticized rayon flock for the base furnish, the shrinkage over the dryers was materially reduced. The total shrinkage was very little greater than that of ordinary paper making fibers and no difficulty whatsoever was experienced in drying the N-10 paper. It is possible that half as much causticized rope would be adequate to control the shrinkage.

It is more difficult to evaluate properly the mechanical strength of the N-10 paper. Whereas the tensile strength in the machine direction did not exceed one pound per inch width, the paper handled much more satisfactory on the paper machine and rewinder than other similar papers having higher tensile strengths. Perhaps this is due to the long rope fibers which contributed some degree of stretch to the paper. The paper showed average scuff resistance, but the folding characteristics were excellent.

The average efficiency of the N-10 paper made from unjordaned stock was over 3.25 percent. Although previous reports on rayon-type papers have shown efficiencies as high as 4.00 percent, there is reason to doubt that this high efficiency could be realized on 100 percent rayon furnish causticized under the present conditions of temperature. With this fact taken into consideration, it is considered significant that causticized rope can be substituted for up to 50 percent of the causticized rayon with no more sacrifice in efficiency than indicated.

It should be pointed out again that the choice of using as much as 50 percent causticized rope fibers was arbitrary. No doubt a lesser amount (like 25 percent) would aid considerably in controlling the shrinkage on the paper machine and would also improve the handling and folding properties.

Further work with this mixed fiber furnish is suggested. Also, further work will be necessary to study more completely the rayon causticizing treatment in the range of 80°F if this type paper is to be made during the summer months.

* * *